

UNIV. OF
TORONTO
LIBRARY



Digitized by the Internet Archive
in 2008 with funding from
Microsoft Corporation

THE CHEMICAL NEWS, FEBRUARY 23, 1912

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

VOLUME CIV.—1911.

LONDON:

PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCXI.

122627
18/6/12

CHEMICAL NEWS, }
Feb. 23, 1912 }

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGDON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME CIV.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

No. 2693.—JULY 7, 1911.

ON THE PREPARATION OF ACETAMIDE.*

By M. A. ROSANOFF, LOUISE GULICK, and H. K. LARKIN.

1. Methods Used Hitherto.

ACETAMIDE has long been prepared by the action of aqueous ammonia upon ethyl acetate, as originally proposed by Dumas, Malaguti, and Leblanc (*Comptes Rendus*, 1847, xxv., 657). The reaction mixture has no effect upon iron, and so the process can be carried out on a considerable scale in iron autoclaves.

The preparation of amides from the ammonium salts of the corresponding acids was first introduced by Dumas (*Ann. Chim. Phys.*, 1830, [2], xliv., 142). The details of this method, as now generally employed for the preparation of acetamide on a laboratory scale, were worked out by Hofmann (*Berichte*, 1882, xv., 977). Hofmann sums up the condition of the preparative method at the time he undertook its amelioration in the following words:—

"If, however, the preparation of amides by treating esters with ammonia leaves much to be desired, the yields obtained by the distillation of ammonium salts are even less satisfactory. Experiments on the preparation of acetamide by this method have been published by Kündig (*Ann. Chem. Pharm.*, 1858, cv., 277), who obtained, in the most favourable case, using glacial acetic acid saturated with ammonia gas, something over 25 per cent of the theoretical yield. In all these distillations streams of ammonia escape at first, which naturally reduces the yield of amide. Petersen (*Ann. Chem. Pharm.*, 1858, cvii., 331), who, at Bunsen's suggestion, modified the experiment by distilling a mixture of equivalent quantities of fused sodium acetate and sal ammoniac, states that acetamide may thus be easily and advantageously prepared, but says nothing concerning the percentage yield. When this experiment was repeated perfectly pure acetamide was obtained directly, but in this case too a large quantity of ammonia was lost, and the final yield of acetamide amounted to only 20 per cent of theory."

Hofmann's method, as given in its optimum form by Gattermann ("Practical Methods of Organic Chemistry," trans. by Schober, New York, 1907), consists in neutralising 75 grms. of acetic acid with ammonium carbonate and heating in sealed tubes for five hours at 225°. The reaction product is subjected to fractional distillation; the fraction passing over between 180° and 230° is collected separately, and on solidification pressed out on a drying-plate. The pressed out crystals are re-distilled, yielding about 40 grms. of almost pure acetamide.

* This operation, however, cannot be carried out on a

large scale. We quote from Hofmann (*loc. cit.*, p. 981):—"Unfortunately this operation cannot be carried out, like the treatment of esters with ammonia, in iron autoclaves, as these are strongly attacked. Acetamide will, therefore, be best prepared in the future, as heretofore, by treating the ester with ammonia at ordinary temperatures."

One or two modifications of the Hofmann method have been proposed since 1882. Schultze (*Journ. Prakt. Chem.*, 1883, xxvii., 512) warms ammonium acetate with acetic anhydride, using no less than 130 grms. of anhydride to 100 grms. of the acetate. This, however, is not only costly, but unquestionably yields much diacetamide together with acetamide. Keller (*Journ. Prakt. Chem.*, 1885, xxxi., 364) distils ammonium acetate in a current of ammonia. We have tried out this method, but with no satisfactory results; unless one carries out a great many re-distillations, which is disproportionately laborious, the yield is very small (generally about 12 per cent of theory).

2. New Method.

Hofmann's method has two disadvantages:—First, the acetate must be heated in sealed vessels; secondly, iron vessels cannot be employed.

From the view-point of chemical statics, there is very little advantage in raising the temperature to 220°. According to Menshutkin (*Journ. Prakt. Chem.*, 1884, xxix., 445) the maximum percentages of acetamide formed at different temperatures are as follows:—

Temperature.	Maximum per cent acetamide formed.
125°	75.1
140	78.2
155	81.5
182.5	82.8
212.5	84.0

Obviously, almost as much acetamide could be obtained at 140° as at 220°. The reason that the higher temperature is generally employed is that at lower temperatures the reaction is impracticably slow.

This suggested the possibility of rendering the old method simple and convenient by employing a *suitable catalytic agent*.

The most appropriate catalyst, apparently, was suggested by the following simple considerations. From the fact that the hydrolysis of amides is catalysed by acids, the inference was drawn that acids would also hasten the opposite reaction, *i.e.*, amide formation. Mineral acids could not be used as they would take up the ammonia from the ammonium acetate. Organic acids generally would yield their own amides in addition to acetamide. *Acetic acid alone could do no harm, and might be confidently expected to promote the reaction catalytically.*

* Contribution from the Chemical Laboratories of Clark University, Worcester, Mass.

Theoretically it was also clear that, by increasing the volume of the reacting mixture, the acid catalyser would improve the yield, since the reaction involves the formation of two molecules (amide and water) from a single molecule (ammonium acetate). This might be expected to counterbalance the slight diminution of yield produced by the temperature lowering.

Experiment soon showed that in the presence of an excess of acetic acid the amide formation really took place with considerable velocity in open vessels. It remained to determine the essential details of the preparation, and this required a large number of trials. The following directions will be found to yield satisfactory results.

First, good dry ammonium acetate is prepared by neutralising glacial acetic acid with pulverised ammonium carbonate at about 50°, allowing to cool, draining off the crystals, and pressing them out twice or three times with filter-paper. The product so obtained contains very nearly 98 per cent of the pure salt.

(NOTE.—The use of ammonium acetate freed from water is best for the obvious reason that water promotes hydrolysis of the amide, and hence necessarily diminishes the yield. Commercial ammonium acetate contains more or less free acid and is unreliable, unless neutralised and pressed out afresh).

100 grms. of this ammonium acetate (corresponding to 75 grms. of acetic acid) and 113 grms. glacial acetic acid (ratio: 1 mol. acetate to 1.5 mols. acid) are boiled in a one-litre flask, with reflux condenser, for five hours. The product is rapidly distilled over with minimum loss and subjected to fractionation (again out of a one-litre flask) with the aid of a two-bulb Wurtz stillhead. (This distillation materially improves the yield). *This operation should be carried out as slowly as possible.* Three fractions are collected separately: (1) the fraction passing over below 180°; (2) the fraction passing over between 180° and 213°; (3) the fraction passing over above 213°. During the distilling of fraction 3 the stillhead is unnecessary. The second fraction (180—213°) is slowly re-distilled with the Wurtz stillhead, and the portion passing over above 213° is added to fraction 3, the remainder being added to fraction 1. The original product is thus divided into a low-boiling and a high-boiling fraction. The former may again be neutralised with ammonium carbonate, and the resulting salt used for a new preparation. The high-boiling fraction, on thorough solidification, is twice pressed out with filter-paper. The dry crystals (practically pure acetamide) weigh over 60 grms., or 20 grms. more than the product obtained by the use of sealed tubes according to the Hofmann-Gattermann directions. The yield is, however, slightly variable, depending on the quality of the ammonium acetate used and especially on the care with which the fractionation is carried out.

(NOTE.—In two consecutive preparations carefully carried out in this Laboratory by Mr. H. R. Godfrey, the yields were respectively 62 grms. and 63.5 grms. At the suggestion of Prof. William A. Noyes, Mr. Godfrey was also requested to try the preparation of acetamide from ammonia and an excess of acetic acid directly, without isolating the ammonium acetate). Dry ammonia gas was introduced into 188 grms. Kahlbaum's glacial acetic acid (= 75 grms. + 113 grms. excess, as above) until the increase in weight amounted to 21.3 grms. This was changed to acetamide according to our directions. Two such consecutive trials yielded respectively 63.3 grms. and 62.2 grms. acetamide. The simplification will be valuable when only one preparation is to be carried out).

It is obvious that the above directions permit of transforming ammonium acetate into acetamide on as large a scale as may be desired, and ought to lead to a considerable reduction of the present price of acetamide, and in order to make certain that the low temperature employed did not after all materially diminish the yield, some experiments were carried out on the following plan:—100 grms. of our fairly dry ammonium acetate and 113 grms. of acetic acid were heated for three hours (experiments

have shown that even two hours would have sufficed) at 225° in sealed tubes. The product was subjected to fractional distillation as described above. The yield was about 56 grms. There is certainly no advantage in using sealed tubes.

Our product boils at 214—216°, which shows it to be nearly pure acetamide.

Clark University, Worcester, Mass.,
March, 1911.

A STUDY OF THE FRUIT OF THE *SOLANUM DULCAMARA*.

By BENTON R. ANDERSON.

REEDER (CHEMICAL NEWS, xcvi., 199) gives analysis of the fruit of *Solanum dulcamara*. His results were mainly qualitative, so it occurred to us it might be profitable to make a more quantitative study of the fruit of this interesting species.

The *Solanum dulcamara*, or woody night-shade, a native of Europe, was introduced into the United States soon after the discovery of America. The flowers of this plant resemble the potato, but are smaller. The fruit is a red ovate berry, and, on account of its luscious appearance, is often eaten by accident.

The berry is quite sweet owing to the large content of sugars. When burned, it gives off three distinct odours; first, an odour similar to that of boiling molasses; secondly, an odour resembling burnt sugar; lastly, an odour of burning wood. The fruit is easily crushed in an agate mortar. There were 304 grms. of berries available for the analysis, which were obtained in August, 1906, at Sylvan Beach, New York. The average weight of a berry was 0.125 gm.

The Sugars.

200 grms. of the fruit were used in the sugar extraction. They were placed in a litre flask, fitted with an inverted condenser, and were treated with boiling alcohol for 250 hours. Each day the alcohol was removed and a fresh portion supplied. The alcoholic extract was distilled off, leaving a thick syrup in the flask.

The process was continued for thirty days; at the end of this time the extract failed to reduce Fehling's solution. The colour of the alcoholic extract was a deep wine colour, but at the end of thirty days the extract was almost colourless, and distilled water was substituted for the alcohol. The berries had remained firm, but soon became mushy under the water treatment. The water extract did not show a clear wine colour, but was black and muddy. Fourteen days more were required to remove all colouration and the remainder of the sugars.

The percentage of the sugars was determined by the reduction of Fehling's solution. The solution was standardised, and it was found that 10 cc. were completely reduced by 0.05 gm. of sugar. 1.5 cc. of the litre solution of the alcoholic sugar extract was added to 50 cc. of boiling water, and titrated with the Fehling's solution. The end-point of the reaction was determined by filtering a small portion from time to time, and pouring the filtrate back until the sugars had no more reducing power. The filtrate was a straw colour until the end-point was reached, when it became a bright blue. The change in colour could be brought about either way by the addition of three drops of Fehling's solution or the same of the sugar solution, so the test appeared to be satisfactory. The water extract was determined in exactly the same manner. There were found to be 61.0 grms. of sugar in the alcoholic extract and 1.05 in the water extract. As 200 grms. of berries were used in the extractions, the above weights correspond to 31.55 per cent of sugar.

The two portions were evaporated to dryness, and the odour resembled burnt sugar. The residue was black and gummy, having the sweetish taste of the original berry.

A part of the residue was treated with distilled water and bone-black. The solution after being filtered out had the red colour of the alcoholic extract. It was evaporated to dryness for treatment with the phenylhydrazine-hydrochloride. A mixture of 2 cc. of distilled water, 0.01 gm. sugar, 0.04 gm. phenylhydrazine, and 0.03 gm. sodium acetate were put in a test tube, and the tube placed in a boiling water-bath. The time required for the osazone formation was taken. Several tests pointed to fructose.

A loss of 46.05 per cent was found when the berries were dried and weighed after the extractions. The berries were reduced in size, and were much shrivelled.

The Oils.

The dried berries from the sugar extraction weighed 106.7 grms. These were placed in a litre flask fitted with an inverted condenser, and were treated with ethyl ether. Three hundred and fifty hours were required to extract the oils. The ether was removed from the extract by distillation. The oils were then purified with bone-black and ether, using a flask and inverted condenser. The purified oil was a beautiful amber colour, and quite viscous. The specific gravity was found to be 0.9603.

The saponification of the oil was made according to the Koetstorfer's method. The oil was very difficult to saponify, four days being necessary. Several saponifications were made in shorter time, but the numbers were much too high. The equivalent was found to be 306. 1.0103 grms. of oil required 3.3 cc. of NaOH. The figures indicate that it is one of the castor-oil group. After the removal of the unsaponifiable portion with ether, the acids were separated. They were principally ricinolic acid, according to the descriptions in the text-books. Each berry has four small seeds which contain the oil. The total weight of the oil extracted was 18.3138 grms. from the original 200 grms. of berries, equivalent to a total of 9.1569 per cent.

The Proteins.

A few of the fresh berries were crushed and boiled in distilled water. A small portion of this extract was heated and nitric acid added. A yellowish tinge showed a trace of albumen.

The nitrogen was determined by the Kjeldahl method. Two grms. of berries were treated, and the analysis showed 0.01868 gm. of nitrogen, equivalent to 0.934 per cent.

The Acids.

The acid tests were made from the sugar extraction, after the purification with the bone-black. A portion of the extract was heated in a beaker glass, and ammonia and calcium chloride were added. The small precipitate which appeared was filtered cold to allow the citrate to pass through. The precipitate was soluble in acetic acid, and so constituted the test for tartaric acid. A portion of the extract was added to a solution of caustic soda, and lime-water was added. When heated a precipitate formed, indicating citric acid. Acetic acid was present, probably due to fermentation.

The Alkaloids.

A modified Dunstan and Ransom's method was used for this analysis. A few grms. of the alcoholic extract were warmed with dilute hydrochloric acid, then filtered and washed with hot hydrochloric acid. The filtrate was shaken in a stoppered cylinder together with a few centimetres of chloroform. The chloroform was then poured off, and evaporated on the water-bath. The pure alkaloid was left in the crucible. It weighed 0.003 gm. This was from 10 cc. of the litre solution of the extract from the original 200 grms. of berries. This amounted to 0.15 per cent. According to Allen's "Organic Analysis" the alkaloid seemed to be an isomer of atropine, *Solanin*.

The Ash.

Four portions of about 2 grms. each were ashed in a 100 cc. platinum dish. From the first portion a dolomite analysis was made, silica, iron, alumina, calcium, and

magnesium being determined. From the second portion the alkalis were determined by a modification of the J. Lawrence Smith method. From the third portion the sulphates were determined by precipitation with barium chloride. The fourth portion was used for the phosphate determination, the magnesia mixture being used to precipitate the acid. The results were as follows.

First Portion.—Weight of Berries, 2.1995 grms.;
Weight of Ash, 0.1143 gm.

	Per cent.
SiO ₂	10.14
Fe ₂ O ₃	6.87
Al ₂ O ₃	7.78
CaO	7.43
MgO	1.73

Second Portion.—Weight of Berries, 2.1425 grms.;
Weight of Ash, 0.1122 gm.

	Per cent.
K ₂ O	11.69
Na ₂ O	9.87

Third Portion.—Weight of Berries, 1.9838 grms.;
Weight of Ash, 0.1029 gm.

	Per cent.
SO ₃	21.67

Fourth Portion.—Weight of Berries, 2.0919 grms.;
Weight of Ash, 0.1085 gm.

	Per cent.
P ₂ O ₅	13.46

Tests were made for chromium and manganese. Traces of manganese were found, but the amount was too small to measure.

The total is 90.73 per cent of the ash. The remainder is organic matter which could not be oxidised and a small amount of carbon dioxide.

After the sugar and oil extractions had been made an analysis was made of the residue. The results in every case were almost the same as the above. A much larger bulk of the residue was needed to weigh out a gm. One gm. ashed weighed 0.0116 gm., as compared with 0.0519 before the extraction of the sugars and oils.

I desire to express my thanks to Dr. Knight for his valuable help in this analysis.

Cornell College Laboratory,
June 1, 1911.

TWO SIMPLE FORMS OF GAS-PRESSURE REGULATORS.*

By EDGAR STANSFIELD, M.Sc.

SOME years ago, when working at the Sunderland Technical College, the writer required a gas-pressure regulator which should give a pressure, steady but easily adjusted, not influenced by the rate of flow of the gas. As he was not able to find any description of a suitable regulator which could be easily made without considerable skill in glass blowing or the purchase of special fittings, he devised two such regulators; these have since proved so useful that it seems desirable to publish a description of them.

In each pattern there is:—

1. An outer vessel; such as a battery jar or wide-mouthed bottle.
2. An inner cylinder, open at the bottom and top; this may consist, as in Fig. 1, of a cylindrical vessel with one or more holes drilled through the sides near the bottom, or, as in Fig. 2, of a wide-mouthed glass bottle with the bottom cut off. A piece of wide glass tubing could be used.

* A Paper read before the Faraday Society, May 2, 1911.

3. A float; a flask, test-tube, or beaker may be used, weighted at the bottom to cause it to float upright. A beaker, as shown in both figures, gave the best results; the rim of the beaker should be an easy fit inside the cylinder.

4. Gas inlet and outlet tubes.

5. A valve connected to the float.

In model A this valve consists of a small bulb blown at one end of a glass tube, the other end of which is fixed in a cork in the neck of the beaker float; the valve seating is a short bit of glass tubing; if the end of this tubing is first made square by rubbing on emery cloth, a very few minutes' grinding of the valve on its seating will then make it almost air-tight. The arrangement of the valve-seating in a cork in a slightly wider glass tube, connected at one

sistent with free movement. A piece of glass tube with a cork in it, in which the rod is fixed, will furnish a suitable cap. The working of the regulator is virtually the same as with model A; in practice the valve would, as a rule, be slightly lower down than is shown in the figure.

In constructing a regulator, unless the inner vessel and accessories are heavy, they should be fixed in the cork of the outer vessel as in Fig. 2, otherwise the buoyancy due to the gas displacing water will cause them to upset. The area of cross-section of the float should be large compared with that of the valve, in order that the pressure exerted on the top of the valve by the inlet gas should be negligible, otherwise a large excess of inlet over outlet pressure may cause the valve to close and remain closed.

Of the two types, A gives a very constant pressure, and if the valve is well ground the flow can be reduced almost

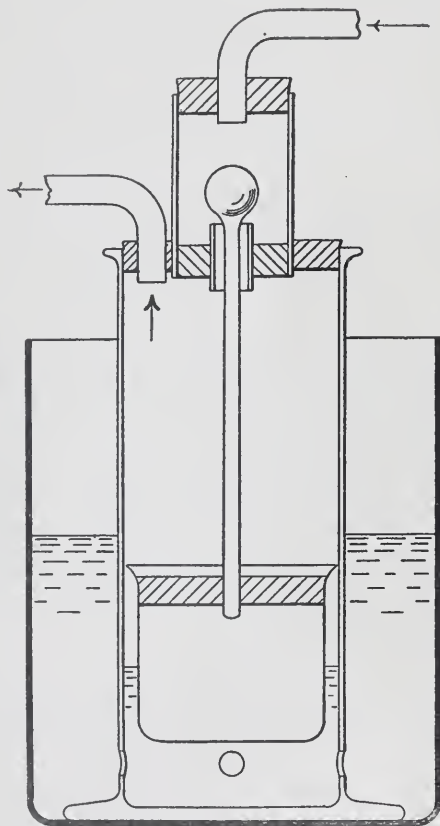


FIG. 1.

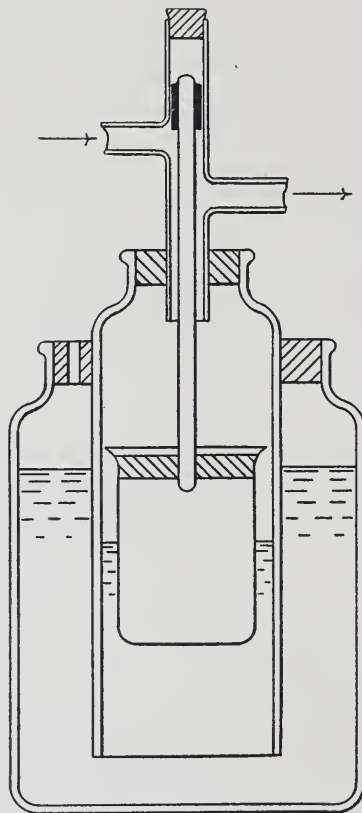


FIG. 2.

end with the gas supply pipe and at the other end passing through a cork in the cylindrical vessel, is obvious from the drawing.

In setting up the apparatus, water is poured into the outer vessel; when gas is passed through in the direction shown by arrows it meets with no resistance until the pressure of gas in the inner vessel causes the water level, and consequently the beaker, to sink, and so closes, or nearly closes, the valve. If the initial pressure is high enough, the pressure in the inner vessel, that is, the gas delivery pressure, will be maintained constant at an amount equal to the difference of water level in the two vessels when the valve is just closing. Pouring water into the outer vessel will give a higher pressure, taking it out will reduce it.

In model B the inlet and outlet tubes have to be blown into a vertical tube; the valve is a glass rod fixed in the cork of the float at one end and having a cylindrical cap at the other which fits in the vertical tube as closely as is con-

to nothing. Its disadvantage consists in the fact that a sudden change of flow may set up a vibration which will keep on more or less indefinitely. In ordinary use with a gas oven, for example, this rarely or never occurs; it could probably be obviated by a slight modification of the shape of the valve.

Model B has a less positive cut-off of the gas, so that it does not give such a constant pressure as A, and the flow of the gas cannot be reduced below the point where it becomes comparable with the leak past the valve; but for a large flow of gas where an absolutely constant pressure is not required, as, for example, for a combustion furnace, it gives very satisfactory results, and it never vibrates like model A. For any definite flow the pressure remains constant, but an increase of flow will slightly decrease the pressure.

Mines Branch, Department of Mines,
Ottawa, Canada.

EIGHTEENTH ANNUAL REPORT
OF THE COMMITTEE ON ATOMIC WEIGHTS.
DETERMINATIONS PUBLISHED IN 1910.*

By F. W. CLARKE.

DURING 1910 a number of important papers on atomic weights have appeared, and their results are summarised in the following pages. A third edition of Clarke's "Recalculation of the Atomic Weights," revised and much enlarged, was published by the Smithsonian Institution early in the year. The new data are as follows:—

Hydrogen.

Atomic weight re-calculated by Grinnell Jones from all the trustworthy determinations (*Journ. Am. Chem. Soc.*, xxxii., 513). The value finally deduced is $H = 1.00775$. That found in Clarke's re-calculation is 1.00779. The two agree to within one part in 25000.

Nitrogen.

Guye and Drouguine have determined the atomic weight of nitrogen from analyses of weighed quantities of N_2O_4 (*Journ. Chim. Phys.*, viii., 473). A spiral of iron wire was heated electrically in the gas, and its increase in weight gave the amount of oxygen contained in the latter. The figures are as follows:—

Weight N_2O_4 .	Weight $2O_2$.	Weight N_2 .	At. wt. N.
0.8856	0.6160	0.2696	14.005
1.8494	1.2860	0.5634	14.019
2.1281	1.4801	0.6480	14.010
1.7191	1.1057	0.5234	14.008
0.9951	0.6921	0.3030	14.010
1.5324	1.0658	0.4666	14.009
1.2425	0.8642	0.3783	14.008
Mean			14.010

Clarke's combination of all previous determinations gives $N = 14.0101$. Richards's value is distinctly lower.

Silver and Iodine.

The ratio between silver and iodine has been re-measured, with extreme care, by Baxter (*Journ. Am. Chem. Soc.*, xxxii., 1603). The corrected weights and ratio are subjoined.

Weight I.	Weight Ag.	Ratio Ag : I.
9.00628	7.65468	0.849927
13.45067	11.43179	0.849905
11.86648	10.08571	0.849933
8.52461	7.24498	0.849890
6.42840	5.46351	0.849902
8.30266	7.05641	0.849897
9.95288	8.45904	0.849909
6.97131	5.92591	0.849899
9.38852	7.97927	0.849897
6.56811	5.58231	0.849911
18.87136	16.03902	0.849913
17.84091	15.16249	0.849872
14.95666	12.71170	0.849902
Mean		0.849906

This mean, combined with that found by Baxter and Tilley for the ratio $2Ag : I_2O_5$, 0.64230, gives $Ag = 107.864$ and $I = 126.913$ (see "Seventeenth Report," *Journ. Am. Chem. Soc.*, xxxi., 257). These values are remarkably low.

Lithium.

The peculiar merit of the work done by Richards and Willard (*Journ. Am. Chem. Soc.*, xxxii., 4) on the atomic

weight of lithium, apart from its accuracy, is found in the fact that the ratios measured give values for Ag, Cl, and Li which are independent of all previous investigations. Three ratios were measured: $LiClO_4$ to $LiCl$ (or $4O : LiCl$), Ag to $LiCl$, and $AgCl$ to $LiCl$. To economise space I omit the "preliminary" series of determinations, and give below only those marked "final." Vacuum weights are given throughout.

Ratio $4O : LiCl$.

Weight $LiClO_4$.	Weight $LiCl$.	Ratio.
12.79265	5.09744	1.50962
10.55416	4.20534	1.50970
11.39912	4.54205	1.50969
11.17008	4.45070	1.50974
17.84842	7.11167	1.50974
22.58273	8.99846	1.50962
Mean		1.50968

Ratio $LiCl : Ag$.

Weight $LiCl$.	Weight Ag .	Ratio.
5.82422	14.82035	0.392988
6.28664	15.99687	0.392991
5.82076	14.81122	0.392997
6.70863	17.07038	0.392998
6.24717	15.89620	0.392998
7.75349	19.72977	0.392984
7.99108	20.33415	0.392988
Mean		0.392992

Ratio $LiCl : AgCl$.

Weight $LiCl$.	Weight $AgCl$.	Ratio.
6.28662	21.25442	0.295779
5.82076	19.67873	0.295790
6.70863	22.68030	0.295791
6.24717	21.12073	0.295784
5.50051	18.59600	0.295790
8.34521	28.21438	0.295779
6.65987	22.51564	0.295789
Mean		0.295786

From these ratios, combined, $Ag = 107.871$, $Cl = 35.454$, and $Li = 6.939$. The authors regard the value for silver as representing the lower limit for that constant. (Scheuer, *Journ. Chim. Phys.*, viii., 289, discusses the atomic weight of chlorine as deduced from the density of HCl . The paper is practically a reproduction of one cited last year. Hinrichs, *Comptes Rendus*, cli., 513, argues that $Ag = 108$ exactly).

Calcium.

Atomic weight re-determined by Richards and Hönigschmidt, from analyses of calcium bromide (*Journ. Am. Chem. Soc.*, xxxii., 1577; a second paper by the same authors is in the *Journ. Am. Chem. Soc.* for January, 1911). Two ratios were measured, with the following results. Vacuum weights are implied. Values calculated with $Ag = 107.88$. $Br = 79.916$.

Ratio $CaBr_2 : 2Ag$.

Weight $CaBr_2$.	Weight $2Ag$.	At. wt. Ca.
4.20860	4.54252	40.068
4.58644	4.95025	40.071
5.34866	5.77301	40.068
7.23724	7.81126	40.073
4.67673	5.04779	40.068
7.41636	8.00455	40.074
Mean		40.0703

* *Journal of the American Chemical Society*, xxxiii., No. 3.

Ratio $\text{CaBr}_2 : 2\text{AgBr}$.

Weight CaBr_2 .	Weight 2AgBr .	At. wt. Ca.
10.18591	19.13778	40.073
7.92400	14.88810	40.072
6.78048	12.73961	40.072
6.45970	12.13702	40.070
5.95390	11.18684	40.067
5.15998	9.69513	40.067

Mean 40.0702

Why this determination, which confirms the earlier work of Richards, should be so much lower than that of Hinrichsen is unexplained. The new work is probably to be preferred.

Strontium.

Thorpe and Francis have re-determined the atomic weight of strontium by several distinct methods (*Proc. Roy. Soc.*, A, lxxxiii., 277). The corrected weights are given in the following summary of results:—

Ratio $\text{SrBr}_2 : 2\text{Ag}$.

Weight SrBr_2 .	Weight 2Ag .	Ratio.
1.77884	1.55073	1.1471
1.86109	1.62260	1.1470
1.85254	1.61511	1.1470
1.73801	1.51534	1.1470
1.85787	1.61994	1.1469
1.70563	1.48707	1.1470

Mean 1.1470

Hence $\text{Sr} = 87.645$.

Ratio $\text{SrBr}_2 : 2\text{AgBr}$.

Weight SrBr_2 .	Weight 2AgBr .	Ratio.
1.86112	2.82438	0.65895
1.85261	2.81155	0.65893
1.73807	2.63762	0.65895
1.85798	2.81099	0.65886
1.70571	2.58866	0.65892

Mean 0.65892

Hence $\text{Sr} = 87.653$.

Ratio $\text{SrCl}_2 : 2\text{Ag}$.

Weight SrCl_2 .	Weight 2Ag .	Ratio.
1.64759	2.24203	0.73486
1.66352	2.26356	0.73491
1.53462	2.08817	0.73491
1.64619	2.24011	0.73487
1.76006	2.39486	0.73493
1.56224	2.12572	0.73492

Mean 0.73490

Hence $\text{Sr} = 87.642$.

Ratio $\text{SrCl}_2 : 2\text{AgCl}$.

Weight SrCl_2 .	Weight 2AgCl .	Ratio.
1.64764	2.97899	0.55309
1.66357	3.00762	0.55312
1.53467	2.77416	0.55314
1.64624	2.97653	0.55307
1.76010	3.18202	0.55314

Mean 0.55311

Hence $\text{Sr} = 87.645$.

Supplementary determinations were made by determining the ratios $\text{SrBr}_2 : \text{SrSO}_4$ and $\text{SrCl}_2 : \text{SrSO}_4$, as follows:—

Ratio $\text{SrBr}_2 : \text{SrSO}_4$.

Weight SrBr_2 .	Weight SrSO_4 .	Ratio.
7.14570	5.30466	1.3471
7.64281	5.67326	1.3472
9.86072	7.32047	1.3470

Mean 1.3471

Hence $\text{Sr} = 87.629$.

Ratio $\text{SrCl}_2 : \text{SrSO}_4$.

Weight SrCl_2 .	Weight SrSO_4 .	Ratio.
7.30246	8.46071	0.86310
8.71628	10.09868	0.86311
8.46493	9.80743	0.86311
8.79502	10.18959	0.86314

Mean 0.863115

Hence $\text{Sr} = 87.661$.

The authors adopt 87.65 as their final value, after discussing the relative merits of the several ratios. The calculations are based upon $\text{Ag} = 107.88$, $\text{Cl} = 35.46$, $\text{Br} = 79.916$, and $\text{S} = 32.07$.

Mercury.

Easley has continued his research upon the atomic weight of mercury, the first part of which was noticed last year (*Journ. Am. Chem. Soc.*, xxxii., 1117). Mercuric chloride was analysed by electrolysis, giving the subjoined results. The weights are reduced to a vacuum, and the calculations are based upon $\text{Cl} = 35.46$.

Weight HgCl_2 .	Weight Hg .	At. wt. Hg .
--------------------------	----------------------	-----------------------

Preliminary Series.

10.05743	7.43123	200.68
8.41289	6.21687	200.71
10.99056	8.11897	200.52
10.28282	7.59681	200.58
19.57120	14.46032	200.65

Mean 200.63

Final Series.

8.14695	6.01909	200.61
11.03881	8.15592	200.64
13.48192	9.96129	200.66
11.08026	8.18610	200.60
11.31231	8.35819	200.66
21.44026	15.84060	200.62

Mean 200.63

This confirms the previous work, and seems to prove that the heretofore accepted value for mercury is too low.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., the Duke of Northumberland, K.G., President, in the Chair. Mrs. Tufnell and Mr. Henry G. Turner, J.P., were elected Members.

The Royal Society of Arts and Mine Rescue Apparatus.—The Council of the Royal Society of Arts have awarded the following medals, under the Fothergill Trust, for life-saving apparatus for rescue work in mines and other places where the air is noxious:—A gold medal to Mr. H. A. Fleuss, for the apparatus submitted by Messrs. Siebe, Gorman, and Co. A gold medal to Mr. W. E. Garforth, in recognition of his efforts to perfect and to secure the adoption of rescue apparatus in mines. A silver medal for the "Draeger" apparatus submitted by Mr. Richard Jacobson. A silver medal for the "Meco" apparatus submitted by the Mining Engineering Company.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, June 14th, 1911.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,
in the Chair.

THIS meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

THE PRESIDENT, in opening the proceedings, said:—We are gathered together in this historic chamber to celebrate what has come to be one of the most important festivals in the Calendar of the Chemical Society, the delivery of the Faraday Lecture, the presentation of the Faraday Medal. The high significance of this meeting is most effectively realised if we call to mind the names of the illustrious men who have functioned as Faraday lecturers in the past. Dumas, Cannizzaro, Hofmann, Wurtz, Helmholtz, and Mendeleeff are those who have passed away leaving imperishable memories behind them. Lord Rayleigh, Professor Ostwald, and Professor Emil Fischer, we rejoice to think, still remain great captains of science militant here upon earth. To this distinguished line of Faraday lecturers the Chemical Society has now added another member in the person of Professor Richards, of Harvard, the eminent savant whom we are to have the pleasure and privilege of hearing to-night. Professor Richards requires no introduction from me; his work, his important contributions to science, especially his determination of atomic weights, and his experiments on the compressibility of the elements, are not only well known in this country, but throughout the chemical world. I have great pleasure in calling upon Professor Richards to deliver the Faraday lecture.

Prof. RICHARDS then delivered the Faraday Lecture, of which the following account is an abstract (full report, *Trans.*, 1911, p. 1201):—

The Fundamental Properties of the Elements.

The subject of my lecture to-night concerns the methods and general results of several extended series of investigations, planned with the hope of adding a little to the foundations of human knowledge by means of careful experiment.

Among all quantities worthy of exact measurement, the properties of the chemical elements are surely some of the most fundamental, because the elements are the vehicles of all the manifold phenomena within the range of our perception.

Weight is clearly one of the most significant of these properties. In the exact determination of atomic weights each portion of substance to be weighed must be free from the suspicion of containing unheeded impurities; otherwise its weight will mean little. Every substance must be assumed to be impure, every reaction must be assumed to be incomplete, every measurement must be assumed to contain error, until proof to the contrary can be obtained.

That the atomic weights may be connected by precise mathematical equations seems highly probable; but although many interesting attempts have been made to solve the problem, the exact nature of such relationships has not yet been discovered. It seems to me that the discovery of the ultimate generalisation is not likely to occur until many atomic weights have been determined with the utmost accuracy.

Volume also is important. About twelve years ago, on applying van der Waals's well known equation to several gases, it seemed clear to me that the quantity b is not really a constant quantity, but is subject to change under the influence of both temperature and pressure. But if the quantity b (supposed to be dependent upon the space actually occupied by the molecules) is changeable, are not the molecules themselves compressible? If changes in the bulk of molecules are to be inferred even from gases, may

not the expansion and contraction of solids and liquids afford a much better clue to the relative expansion and contraction of these molecules? Much evidence has been accumulated pointing toward a positive answer to these questions.

The ordinary conception of a solid has always seemed to me little short of an absurdity. A gas may very properly be imagined with moving particles far apart, but what could give the rigidity of steel to such an unstable structure? The most reasonable conclusion, from all the evidence taken together, seems to be that the interstices between atoms in solids and liquids must usually be small, even in proportion to the size of the atoms themselves, if, indeed, there are any interstices at all. The kinetic theory of gases remains unmolested by these considerations, except as they indicate the changeability of b in the equation of van der Waals, but the new views affect seriously the application of this equation to solids and liquids.

The compressibilities of thirty-five elements and many simple compounds were studied with sufficient care to leave no doubt as to their relative values. It became at once manifest that the formation of a compound of a compressible element was attended with greater decrease of volume than the formation of a similar compound of a less compressible element, other things being equal. This is just what the theory leads us to expect, and is a fact inexplicable by any other hypothesis as yet known to me.

Another essential aspect of the theory of compressible atoms is that which concerns cohesion. If the pressure of chemical affinity causes atomic compression, may not the pressure of cohesive affinity also have the same effect? The affinity which prevents solids and liquids from vapourising is generally admitted to produce great internal pressure; must it not tend to compress the molecules into smaller space? Molecules with high cohesive affinity (those of substances hard to volatilise) should be much compressed, and possess small volume, whereas molecules with a slight cohesive affinity should be more bulky. Moreover, those molecules already much compressed by their own self-affinity would naturally be but little affected by additional pressure.

Thus, as regards two substances otherwise similar, the less volatile one would be less compressible, denser, and possess greater surface tension. These outcomes of the theory correspond with the facts in a majority of cases thus far studied. Differences of structure and differences of chemical nature sometimes conceal these relations; the parallelism appears most strikingly among isomeric compounds. In brief, the bulk of evidence strongly indicates that cohesiveness, as well as chemical affinity, exerts pressure in its action, and hence that each plays a part in determining the volumes occupied by molecules.

Carried through to its logical conclusion, the idea that atoms are compressible gives one quite a new conception of the molecular mechanics of the universe. The influence of atomic compressibilities may be perceived everywhere, and in most cases each fact seems to fit easily and without constraint into its place in the hypothesis. Even apparent exceptions, such as the abnormal bulk of ice, may be ascribed in a reasonable fashion to superimposed effects.

The more closely the actual data are studied, the more plausible the hypothesis of compressible atoms appears. Ten years' experience with its interpretations leads me to feel that the idea is highly suggestive and helpful in stimulating new search after truth, and in correlating and codifying diverse facts. By such fruits are hypotheses justified.

Chemical energetics being involved in the consideration of these relations, I sought to improve the technique of thermochemistry. The new method of adiabatic calorimetry was devised, and with it interesting results have been obtained.

All these and other properties of the elements are to be compared with each other quantitatively. New evidence is at hand showing that they do not all vary with the same

periodicity as the atomic weights increase. The solution of the cosmic riddle is of the greatest importance to humanity, because only through a complete understanding of his own structure and that of his environment can man obtain control of the necessary conditions of his existence. The outlook is full of hope for the future.

In presenting the Faraday Medal to Prof. Richards at the conclusion of the lecture, the PRESIDENT said:—Professor Richards, —It is now my pleasant duty, in the name of the Chemical Society, to present you with the Faraday Medal, which bears the effigy of the Master, and which has been struck expressly for this occasion. It is the highest honour which this Society has to confer. In making this presentation I desire to assure you of the sincere appreciation and the deep regard which your colleagues in this country have for your work, and also of the great and enduring importance which we attribute to your scientific discoveries.

Prof. ODLING, in proposing a vote of thanks to the lecturer, said:—Mr. President, Ladies, and Gentlemen,—Some two or three days ago I was highly gratified by being invited to be present by the President, the distinguished son of a distinguished father, to undertake the duty of proposing a vote of thanks to the lecturer. But this gratification, I find now, is sadly marred by the sense of my utter incompetence to express in fitting terms our appreciation for the intellectual treat which has been put before us. At the same time there is, perhaps, a certain inferior fitness in this duty being assigned to me in consideration of my connection with Professor Faraday, as being for a time his successor in this institution, and with the Chemical Society, by which the lectureship has been instituted. At the present time the Fullerian professorship is occupied by Sir James Dewar, who is unfortunately not able to be present with us on this occasion, and whose personal exertions have added so much to the reputation of this professorship. In the time between his acceptance of the professorship and his assumption of office, the professorship was held by myself and by Dr. Gladstone, and this particularly, therefore, brings us into association with the Royal Institution. With regard to the Chemical Society, I am perhaps entitled to speak on its behalf in a double capacity, in that I am at the present time the senior Fellow of the Society, and that the institution of this lectureship was carried out at my personal proposition, and, in some measure, I venture to say, through my personal activity, because, although the proposition met with hearty goodwill, there were some technical difficulties which required to be smoothed over. As the oldest member of the Chemical Society, I may venture to remind you that I was elected in the presidency of Professor Brande, a long time the secretary of the Royal Society and the favourite pupil of Sir Humphry Davy, and the successor of Sir Humphry Davy in his professorship of the Royal Institution, he himself being subsequently succeeded by Faraday. On the institution of this lectureship we were fortunate in securing Dumas as our first lecturer. It was thereby at once recognised that a very high standard of proficiency had been established for the lecturers who would follow him. That standard has been thoroughly well kept up by Professor Richards, to whose admirable and searching address we have listened with so much interest. For myself I would venture to say that I do not feel at all shocked by his proposition as to the absolute continuity of matter in the solid and liquid states. On the occasion of the first Faraday lecture, Dumas enlarged on the absolute unresolvability of what we called the chemical elements, as they were then known. He pointed out that those forms of matter had existed unchanged for millions of years, and suggested that they were likely to remain unchanged for millions of years to come, a suggestion which I would recommend with all deference to Sir William Ramsay. Our present lecturer, Professor Richards, has, we shall all agree, more than attained the high standard which was originally set up. I had the pleasure of hearing Professor Richards at Oxford

a few days ago, and I was much struck by his expression of hopefulness for the future, that there should be no resting places in chemistry, and that the work should go on for ever. If we look back to the time of the institution of the Chemical Society, some seventy years ago, I think we may say there has been no decade in which fundamental points of importance in the way of discovery and interpretation have been lacking, and neither has continuity failed. On the occasion to which I have referred, Professor Richards enlarged on the fact that, so far from having passed the grand age of chemistry, we were really after all only at the beginning. That is the feeling which must animate all of us. When the Faraday Lectureship was instituted, it was with the two-fold object of doing honour to Faraday, and of enabling the Fellows of the Chemical Society to meet and hear the views of the most eminent men among foreign professors. That Professor Richards possesses the qualification of eminence goes without saying, but that he possesses the qualifications of being a foreigner may be very much doubted. Here we do not recognise the citizens of the United States, and more particularly the scientific men of the United States, with many of whom it has been my advantage to be associated, as being in any way foreigners. We are pleased to greet them, and Professor Richards is one of ourselves. At the present moment we have the Professors of Chemistry at Harvard and Yale on our list of Honorary Fellows, and a number of other illustrious citizens of the United States whom we are proud to consider as being part and parcel of ourselves.

Sir WILLIAM TILDEN:—Mr. President, Ladies, and Gentlemen,—I rise very willingly to second the resolution which has been laid before the meeting by our senior Fellow. But, as might be expected when you think that Dr. Odling was asked to move the resolution, you will see that he has exhausted the subject. However, I, too, have enjoyed the privilege of being present on a good many occasions when the Faraday Lectures have been given in this room, and, though, of course, I was very young at the time, I quite distinctly remember the magnificent discourse given by Dumas. I remember also that, in his peroration, he seemed to indicate that there was some sort of limit set, either by human capacity or in some other way, to the possibilities of science, but if he had lived, as we have had the advantage of doing, down to the beginning of the twentieth century, he would no doubt have changed that opinion fundamentally. However, Professor Dumas was, at the time of the Faraday Lecture in 1869, almost at the end of his career, and he did not live many years after that. Our Faraday Lecturer to-night has led us to look forward with a hopeful feeling to the development of new ideas in chemistry and physics. He is still a young man, and, as we hope, not half-way through his magnificent career. In seconding the vote of thanks, I should be glad to be allowed to express in your name our most cordial wishes for the continuance of his good health, good spirits, and strength, to carry on those laborious experiments with which we are all familiar on this side of the Atlantic. In listening to his discourse, it was with a feeling of mingled relief and disappointment that I found he was talking about the fundamental properties of the elements without having given us the definition of an element. I gathered with some satisfaction that he was really referring to the old-fashioned elements which were talked of by Dalton and others, and which are referred to in the well-known classification of the elements in the Periodic Table. For my part, I am afraid I am too old to learn the new sort of chemistry which seems to be coming up, but I do feel very strongly that we are not likely to part with our old friends the Daltonian elements—whether they are preserved or not I do not care—so long as the wonderful development of stereochemistry in the last few years continues to be evolved. It seems to me that the whole of stereochemistry is the fundamental argument in favour of the stability of atoms in chemical combination. However, this is not the time, nor am I the person, to present these views to you.

I should like to be allowed to support the proposal which has been laid before you so eloquently and in so interesting a manner by Dr. Odling, that we should return to our cousin from the other side of the Atlantic our most cordial thanks for the brilliant and admirable discourse which he has given us to-night.

Prof. DIXON :—Mr. President, Ladies, and Gentlemen,—On looking back at my late tenure of the office of President, which you, Sir, I think, have defined as two years' hard labour, I know there is one pleasurable duty which more than made amends for all the routine duties which fell to my lot in that position, and that was the privilege of conveying the invitation of this Society to the Faraday Lecturer of to-night. The Chemical Society looks high, and it expects much. Professor Richards has more than fulfilled those expectations. We have listened to-night to a story that is more entrancing than any fairy tale, because as we followed the flight of the lecturer's imagination we knew that that flight was surely guarded and controlled by a man who had measured and weighed the elements with an accuracy hitherto unknown. Concerning the weighing of the elements, our old European ideas of finality have been overthrown by Professor Richards and his school, and we are at this moment seeing the fulfilment of the prophecy of Canning when he said, "I look to the new world to redress the balance of the old."

The CHAIRMAN having put the vote to the meeting, it was carried with acclamation.

Prof. RICHARDS :—Mr. President, Ladies, and Gentlemen,—I can hardly find words to express my very deep and heartfelt appreciation, first, of the great honour, the extraordinary high honour, which the Chemical Society has conferred upon me by inviting me to give this lecture and by awarding me this famous Medal, and, secondly, by the most kind expressions of opinion and of good feeling which I have heard here to-night. I shall treasure this Medal always, as a token of your kindness, and I shall, whenever I look at it, think of this memorable evening in this memorable building, where not only the great Faraday, but so many great men, have laboured and lectured.

FARADAY SOCIETY.

Ordinary Meeting, May 23rd, 1911.

Dr. R. T. GLAZEBROOK, C.B., F.R.S., Vice-President, in the Chair.

General Discussion on High Temperature Work.

PREVIOUS to the meeting the Society visited the National Physical Laboratory, by the kind invitation of the Director, and inspected the high temperature equipment described in Dr. J. A. Harker's paper. Mr. H. C. Greenwood gave a demonstration of his method for determining the boiling-points of metals, described in the paper contributed by him to the General Discussion.

After some introductory remarks by the Chairman, Dr. ARTHUR L. DAY, Director of the Geophysical Laboratory, Carnegie Institution, Washington, contributed the first paper to the Discussion, entitled "*Recent Advances in High-temperature Gas Thermometry.*" (Will be inserted in full).

Dr. J. A. HARKER, F.R.S., gave a short abstract of his paper, illustrated by lantern-slides, on "*The High-temperature Equipment of the National Physical Laboratory.*"

The paper dealt with the methods of construction and the use of the various forms of apparatus for the attainment of temperatures above 100° C. which have been designed at the laboratory during the past ten years. For liquid baths the general system adopted throughout, both for these and lower temperatures, consisted in the use of a vessel made up of two parallel vertical tubes, cross connected above and below. In one of these tubes is placed a continuous rotary stirrer, and in the other the apparatus

to be heated. The heating may be by gas or electric current. The baths are so designed that the work to be accomplished by the stirrer in equalising the temperature of the different parts is a minimum, and great uniformity of temperature in the working tube is thus attained. Common olive oil is employed between 50° and 220° C., and above that temperature mixtures of fused salts are used, one of the most convenient being equal molecules of KNO₃ and NaNO₃, which melts at 219° C., gives off no fume, and can be used in an iron vessel as high as about 650° C. Diagrams show the details of the final forms of vessel adopted and the method of heating used in each case.

The construction of electric furnaces for various temperature regimes forms the subject of the second half of the paper, several wire and foil wound furnaces for different purposes being described in detail.

The gradual improvements in the construction of these, in the methods of lagging, are described, and the amount of energy required to reach a given temperature is tabulated for furnaces of very different dimensions.

The construction of the large platinum-wound "black body" radiation furnaces used by Blackie and the author for standardisation of "total-radiation" pyrometers is illustrated by diagrams, and the improvements introduced into this type of furnace, which have greatly increased its useful life, are described.

The construction and use of carbon tube furnaces of different kinds for temperatures up to 3000° C. form the subject of the concluding section of the paper, the spiral furnace of Price and the author being described in detail for the first time. The advantages of the various types of carbon furnace, their suitability for different purposes, and the methods for temperature regulation of the same are discussed.

The whole paper is intended to give sufficient information to enable the various pieces of apparatus described to be constructed and worked successfully by any one desiring to do so.

Mr. H. C. GREENWOOD, M.Sc., read a paper entitled "*The Boiling-points of Metals.*" (Will be inserted in full).

Mr. A. BLACKIE, B.A., communicated a paper "*On the Behaviour of Silica at High Temperatures.*" (Will be inserted in full).

Prof. MAX BODENSTEIN, of Hanover, sent in a communication on "*Methods of Maintaining Constant High Temperatures.*"

Three general methods are in use.

1. By means of a vapour in equilibrium with its liquid. Suitable substances are only available for a moderate range of temperature, but a uniform temperature over a large volume is easily maintained. On the other hand, constancy of temperature over a long period cannot be relied upon.

2. A liquid heating-bath controlled by a thermostat. For high temperatures the method is restricted by the difficulty in obtaining a suitable substance, although for moderate temperatures oil or paraffin in a suitably constructed bath are fairly satisfactory, and temperatures up to 350° can be maintained within 0.05° for several months if a sensitive gas regulator be employed.

3. For high temperatures air-baths only can be employed. Tube furnaces heated electrically, either directly or by means of coils, are now exclusively used, but although a constant temperature is easily maintained, uniformity of temperature is more difficult of attainment. Usually the spiral heating-coil is wound more closely at the ends of the tube, where the heat insulation should also be better, or additional resistances may be placed in front of the ends, and thus the heating of the middle portion of the tube is kept uniform. If there are any fluctuations in the current, it is necessary to employ a thermo-regulator. In the form recommended by the author the expansion of a confined volume of gas moves a column of mercury against a constant gas pressure. The motion of the mer-

cury actuates, by means of a relay, a secondary current superimposed upon the primary heating current. Various modifications of the method are suggested, and it is stated that its use will render possible the maintenance of temperatures up to 1500° C.

M. CHARLES FÉRY contributed to the Discussion a short Note on "*Stellar Pyrometry*."

The temperatures of incandescent terrestrial bodies can be measured by reference to the laws of radiation, either the law of Stefan or the law of monochromatic radiations, but these cannot be applied in the case of stars, owing to the small amount of radiation. The author has therefore devised an instrument based on Weiss's displacement law, according to which temperature is measured by an appreciation of the colour tint of the star. In the instrument described the colour of an image of the star is compared with that of a standard lamp whose tint can be varied. The pyrometer is standardised by reference to an electric furnace, an arc (3500° C.) and the sun (6500° C.).

In the course of the general discussion which followed the reading of the papers—

Dr. T. M. LOWRY suggested the use of helium or argon in high-temperature gas thermometers instead of nitrogen.

Dr. J. A. HARKER agreed that a substitute would have to be found for nitrogen, which was not inactive in the electric furnace. Helium was impracticable, but he thought argon promising. The difficulty was a suitable containing material; they were trying to find one at the National Physical Laboratory.

Dr. ARTHUR DAY threw out the suggestion that tungsten might be found a possible material.

Prof. A. K. HUNTINGTON commented on the distinction which should be drawn between the diffusion of gases through metals, which depended on affinity, and through porcelain, which was merely a matter of porosity.

NOTICES OF BOOKS.

Physico-chemical Tables. Vol. II. By JOHN CASTELL-
EVANS, F.I.C., F.C.S. London: Charles Griffin and
Co., Ltd. 1911. (36s. net).

THE second volume of this comprehensive book of physico-chemical tables contains many lists of data relating to capillarity, surface tension, the physical properties of solutions, and molecular weights. Analytical tables are also included, and very full lists are given of multiplying factors and logarithms for every substance which is likely to be met with in analytical work. Methods of calculation and the use of the tables are fully explained, and it would be a difficult matter to suggest additions or improvements to make the book more complete or convenient in use.

Crystals. By A. E. H. TUTTON, D.Sc., M.A., F.R.S.
London: Kegan Paul, Trench, Trübner, and Co., Ltd.
1911. (5s.).

THIS book is an amplification of the author's Evening Discourse to the British Association at the Winnipeg Meeting held in 1909, and gives a full account of the advances which have recently been made in crystallography. The experiments which were performed at the lecture are described in detail, and the phenomena exhibited by crystals in polarised light are admirably shown in the illustrations. The subject is treated as simply as is compatible with a thorough exposition of its essential features, and technical and mathematical terms are avoided as far as possible. The author's enthusiasm for his subject will inevitably awaken his readers' interest, and his accounts of the early study of crystals, of the work of Mitscherlich, and of liquid crystals are most stimulating. The growth of a crystal from a solvent, and the parallelism of crystal growth and the growth of a living organism is treated in a really fascinating style, the salient points being made exceedingly clear.

The Manufacture of Sulphuric Acid and Alkali. By
GEORGE LUNGE, Ph.D. Third Edition. Volume III.
London: Gurney and Jackson. 1911. (30s. net).

THE third volume of the third edition of this treatise deal with the ammonia-soda process and the chlorine industry, as well as various suggested methods for manufacturing alkali which the author criticises from the point of view of their practicability. Throughout the book the reader meets with shrewd comments upon the usefulness of the different processes reported upon, and the author, keeping in view his special aim of comprehensiveness, has not hesitated to describe in detail a proposed method and then explain the inherent defects which would prohibit its successful adoption. Even obsolete methods which are of historical interest only are included, and much of Prof. Lunge's recent work is discussed.

Inorganic Chemistry. By F. STANLEY KIPPING, Ph.D.,
Sc.D., F.R.S., and W. H. PERKIN, Ph.D., Sc.D., Ll.D.,
F.R.S. London and Edinburgh: W. and R. Chambers,
Ltd. 1911. (7s. 6d.).

THIS text-book of inorganic chemistry, the first part of which has already been reviewed in these columns, provides a continuous three years' course, suitable for students who are beginning the study of the science, and who aim at obtaining a University pass degree. In Part I. the first year's course is given, the chapters being arranged in the order in which the author believes the subject can most profitably be studied, and in the second part the more detailed study of the elements grouped according to the Periodic System is taken up. Throughout the book much space is given to the consideration of the principles and theories of chemistry, and the discussions of theory are exceedingly clear and concise, giving precisely what the average student requires for a proper understanding of the fundamental laws of the science. The theoretical matter includes practically all that can be profitably studied before advanced work is taken up, and the book would want but very little supplementing on this side, though the treatment might be found rather slight from the point of view of descriptive chemistry. An attempt has been made to differentiate between the second and third year's work by running a line down the margin of the more advanced matter, which, however, takes its proper place in the text, so that there is no disturbance of the continuity. The book is one which is likely to be widely adopted, and only a very cursory survey will be necessary to convince both teachers and learners of its merits, which will be made still more conspicuous by constant use.

Die Chemie der Cellulose. ("The Chemistry of Cellulose").
By SCHWALBE. Volume I. Berlin: Gebrüder Born-
traeger. 1911. (9 mk. 60 pf.).

THIS treatise contains a complete summary of all the facts which are known concerning the chemistry of cellulose. Cotton cellulose, as being the most thoroughly studied representative of the class, is considered first, and Part I. of Vol. I. gives an account of its preparation in the pure state and its behaviour towards reagents, including dyes. Among the reagents taken into account are water, acids, alkalis, and oxidising agents, and the effects of heating, of air and light, as well as the results of passing an electric current through suspensions of cellulose, and the fermentation of the substance are all described. The second part of the book deals with the derivatives of cellulose, e.g., its hydrates and oxy-derivatives. Some of the author's as yet unpublished results are included, and very full references are given to the literature of the subject. The book prepares the way for further advances in the scientific knowledge of cellulose, especially as regards its investigation from the point of view of colloid chemistry, from which many important results may be expected.

Themen der Physikalischen Chemie. ("Essays on Physical Chemistry"). By Dr. EMIL BAUR. Leipzig: Akademische Verlagsgesellschaft. 1910. (4 marks).

THESE ESSAYS are based upon lectures which were delivered at the vacation courses for engineers held at the Technische Hochschule at Brunswick, and which were evidently excellently suited for their purpose. They gave in an interesting and succinct form a *résumé* of the results which are the outcome of recent work on the different branches of physical chemistry. No special knowledge of chemistry would be necessary to follow the outlines of modern developments of catalysis, metallography, colloidal chemistry, to mention some of the subjects of the essays, and the fact that the lectures were illustrated by experiments must have added considerably to the interest of the audience and the benefit they derived. Every engineer who can understand German will find that he will gain some new points of view by reading the book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 19, May 8, 1911.

Hydrates of Rubidium and Cæsium Fluorides.—M. de Forcrand.—The following hydrates of rubidium and cæsium fluorides exist:— $\text{RbF} + 1.5\text{H}_2\text{O}$ (m. p. 36°), $\text{RbF} + \frac{1}{2}\text{H}_2\text{O}$, $\text{CsF} + 1.5\text{H}_2\text{O}$, $\text{CsF} + \frac{3}{2}\text{H}_2\text{O}$. The dissociation temperatures are 256° , 178° , 260° , 182° .

Catalytic Decomposition of Formic Acid.—Paul Sabatier and A. Mailhe.—With dehydrogenating catalysts, such as platinum sponge, reduced copper, or zinc oxide, formic acid is decomposed according to the equation $\text{HCO}_2\text{H} = \text{CO}_2 + \text{H}_2$. Dehydrating catalysts, such as TiO_2 , induce the following reaction: $\text{HCO}_2\text{H} = \text{CO} + \text{H}_2\text{O}$, while with mixed catalysts, such as thorium dioxide, the action is $2\text{HCO}_2\text{H} = \text{HCOH} + \text{CO}_2 + \text{H}_2\text{O}$.

Production of Ammonia and Economy of Nitrogen by Peat.—H. Wolterck.—The author treated peat with water vapour alone, and after the formation of ammonia was completed, and the amount of nitrogen had been determined, subjected the residue to the action of a mixture of air and water. Thus it was found that treatment with water alone produced only one-third of the amount of ammonia obtained by the action of a mixture of water and air in the same conditions. Moreover, the amount of nitrogen lost in the action of the vapour corresponded nearly to that recovered in the form of ammonia. No acetic acid is formed by treatment with water alone at 450° , while in presence of air at the same temperature 2.31 per cent of acetic acid is obtained.

Gases contained in Steel.—G. Charpy and S. Bonnerot.—When the gases contained in steel are separated by heating in a vacuum at 950° , it is found that the small amount of water introduced owing to the use of a mercury air-pump and porcelain tubes brings about a reaction with the steel. The volume of gas obtained differs in different specimens of steel, the percentage of carbon monoxide varying from 26 to 32 per cent.

Action of Carbon Oxychloride on Natural and Artificial Sulphides.—Ed. Chauvenet.—At comparatively low temperatures (300 – 450°) carbon oxychloride acts on natural and artificial sulphides, giving chlorides, $\text{MS} + \text{COCl}_2 = \text{MCl}_2 + \text{COS}$. Thus carbon oxychloride can be used to transform sulphides completely into anhydrous chlorides, and a method of opening up and determining natural sulphides can be based upon this process.

Bromination of some Hydroaromatic Derivatives.—F. Bodroux and F. Taboury.—In the dark cyclohexane

is not attacked by bromine, but in sunlight hydrobromic acid is set free and cyclohexyl bromide is formed. It gives with bromine a viscous liquid from which no definite compound can be extracted. Dibromocyclohexane and methylcyclohexene are transformed by bromine in presence of aluminium almost quantitatively into hexabromobenzene, C_6Br_6 . Methylcyclohexane and 1-2- and 1-4- methylcyclohexene give a viscous liquid, and a solid product which consists chiefly of pentabromotoluene. 1-3-Dimethylcyclohexane gives tetrabromxylylene, and from menthene and thymomenthene only viscous liquids are obtained.

Dinaphthothiophene.—M. Lanfry.—When sulphur acts on naphthalene at a red heat a crystalline substance of formula $\text{C}_{20}\text{H}_{12}\text{S}$ is obtained. On oxidation with aceto-chromic solution it gives o-phthallic acid. With bromine it yields a hexabromo derivative, and with boiling nitric acid a tetranitro compound, $\text{C}_{20}\text{H}_8(\text{NO}_2)_4\text{S}$, is formed.

Researches on Oxy-indazols.—P. Freundler.—At a low temperature the ortho-substituted azo-acids give chlorinated oxy-indazols with phosphorus pentachloride. These compounds contain an indazyl nucleus and a hydroxyl group attached to the central carbon. The two chlorine atoms of the nucleus are in the 3 and 5 positions. The OH group confers on the oxyindazols a phenolic character. They are feebly basic, and are characterised by the ease with which they can be converted into the corresponding azo-acids.

Synthesis of Tertiary α -Ketonic Alcohols.—D. Gauthier.—When Blaise's reaction is applied to the cyanides of the acetones, $\text{R}_1\text{R}_2\text{C} > \text{COH} - \text{CN}$, they are transformed into tertiary α -ketonic alcohols of the type $\text{R}_1\text{R}_2\text{C} > \text{COH} - \text{CO} - \text{R}_3$. Thus 2-methyl-2-oxy-3-butanone and its homologues can be prepared. These new ketonic alcohols are distinguished from the corresponding secondary alcohols, $\text{R}_1 - \text{CHOH} - \text{CO} - \text{R}_2$, because even on heating they do not reduce cupro-potassic liquid nor ammoniacal silver nitrate.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 7, 1911.

Root-dye of Azafran.—C. Liebermann.—The author has investigated the dye which can be isolated from the root of a plant belonging to the Scrophulariaceæ and indigenous to Paraguay. The dye is obtained from the roots by means of boiling alcohol or benzene, when it separates in the form of orange-red flakes which melt at 214° . It is soluble in organic solvents, insoluble in water, unaltered by alkalis and ammonia in the cold. When boiled with alkalis or alkaline carbonates it dissolves, giving a yellow solution, from which it is re-precipitated by alkalis. With concentrated sulphuric acid it gives a blue colouration, which changes to violet on the addition of alcohol. The dye, for which the author suggests the name azafrin, contains no nitrogen. On analysis it is found to contain about 75 per cent carbon and 9 per cent hydrogen. No methoxyl or ethoxyl groups are present in it. Its molecular weight lies between 448 and 462, and it contains one hydroxyl group.

Atti della Reale Accademia dei Lincei.
Vol. xx., No. 5, 1911.

Nitropyrrol.—A. Angeli and Luigi Alessandri.—Pyrrol and its derivatives are decomposed by the action of nitric acid, but nitropyrrol can be prepared by adding an atom of sodium and a molecule of ethyl nitrate to a molecule of pyrrol diluted with ether. Thus the sodium salt of nitropyrrol and sodium nitrite are formed, and may be separated by adding a solution of silver nitrate; the silver salt of nitropyrrol, which is thus prepared, together with silver nitrite, is insoluble in water, while silver nitrite is soluble. The silver salt is converted into the sodium salt by the

addition of sodium chloride. A perfectly analogous process gives rise to the formation of nitro- α - β -dimethyl pyrrol.

Decacyclene and its Action on Graphite.—M. Padoa.—Decacyclene can be prepared by heating acenaphthene with sulphur, adding sulphuretted hydrogen, again heating to 250°, and then re-crystallising from nitrobenzene. When graphite was heated with pure decacyclene at 430° a fusion curve was obtained, exactly like that of pure decacyclene, and the graphite remained quite unaltered.

Vol. xx., No. 6.

Silicon Sulphides.—Livio Cambi.—Silicon monosulphide exists in two forms, one orange-yellow and the other black. When the former is hydrolysed the following reaction occurs: $-\text{SiS} + 2\text{H}_2\text{O} = \text{H}_2\text{SiO}_3 + \text{H}_2\text{S}$. The black monosulphide undergoes dissociation, giving the disulphide $2\text{SiS} \Rightarrow \text{Si} + \text{SiS}_2$. This recalls the behaviour of stannous sulphide from which tin and stannic sulphide are formed.

Amorphous Silicon.—Livio Cambi.—The silicon obtained by the dissociation of the black sulphide of silicon may be regarded as amorphous silicon. It differs from the products described by Vigouroux, Hempel, and v. Haasey in physical properties, e.g., in colour and specific gravity. It turns brown when heated.

Luminosity of Phosphorus.—L. Marino and C. Porlezza.—The authors describe an apparatus by means of which the luminosity of phosphorus can easily be demonstrated to a large audience. The hot vapour is carried into a large flask by a current of carbon dioxide, and then appears to generate a beautiful green flame. It is found that when phosphorus is oxidised in oxygen, much diluted with an inert gas, the product is one of the lower oxides, probably P_4O . In excess of oxygen P_2O_5 is formed by the complete combustion of phosphorus, while, when phosphorus is heated in a current of air, P_2O_3 and P_4O are formed.

Existence of New Type of Dioxide.—L. Marino and V. Squintani. When 25 grms. of manganese dioxide are heated to 140° in a closed tube with 70 grms. of selenious anhydride dissolved in 500 grms. of water, a selenite of the dioxide is formed. The compound is orange-yellow coloured, insoluble in water, nitric acid, and dilute sulphuric acid. It is soluble in hydrochloric acid. It liberates iodine from a solution of potassium iodide acidified with acetic acid. With alkaline carbonates and hydroxides, MnO_2 is set free, the decomposition taking place according to the equation $\text{MnSe}_2\text{O}_6 \Rightarrow \text{SeO}_2 + 2\text{SeO}_2$. When heated to 400° at atmospheric pressure the salt decomposes as follows: $-\text{MnSe}_2\text{O}_6 \Rightarrow \text{MnO}_2 + \text{MnSeO}_4$. The manganoous selenate gradually decomposes as the temperature is raised, the whole reaction being represented by the equation $5\text{MnSe}_2\text{O}_6 \Rightarrow 8\text{SeO}_2 + 2\text{MnSeO}_4 + \text{Mn}_3\text{O}_4 + \text{O}_2$. All these results show that the compound MnSe_2O_6 is to be regarded as a selenite of manganese dioxide.

Thermic Analysis of Mixtures of Copper Chloride with the Chlorides of Monovalent Elements.—C. Sandonnini.—The crystallisation curves of mixtures of sodium chloride and copper chloride show a eutectic at 75 mol. per cent CuCl . In the system $\text{AgCl}-\text{CuCl}$, the eutectic occurs at 54.6 mol. per cent CuCl , and with $\text{KCl}-\text{CuCl}$ at 67 mol. per cent CuCl . Thallium chloride gives a compound CuCl_2TlCl , the temperature of formation being 226°. With potassium chloride also a double salt, $\text{CuCl}_2\cdot 2\text{KCl}$, is formed.

Binary Systems of Chlorides of Monovalent Metals.—G. Poma and G. Gabbi.—In this paper the authors give the results of the investigation of the systems $\text{CuCl}-\text{AgCl}$ and $\text{CuCl}-\text{KCl}$, with graphic representations of the fusion curves.

Equilibrium of Solutions of Iodine in Organic Substances.—F. Olivari.—The solubility curve of iodine in the neighbourhood of the melting point of the element is practically the same for iodoform, azobenzene, p -dibromobenzene, and p -dinitrobenzene, while the slope of the

curve is less for benzoic anhydride and benzoic acid. Iodine is not completely miscible with p -dibromobenzene, p -dinitrobenzene, benzoic anhydride, and benzoic acid. There is a point of flexion in the solubility curves with p -dibromobenzene and azobenzene at 70 and 60 per cent respectively.

MISCELLANEOUS.

Royal Society of Arts.—The Annual General Meeting of the Royal Society of Arts took place on June 28th, Sir John Cameron Lamb, C.B., C.M.G., Chairman of the Council, presiding. The Annual Report shows that the office of President has now been accepted by H.R.H. the Duke of Connaught. Up to the death of King Edward VII. it was occupied by H.R.H. the Prince of Wales (King George V.), and, on his accession to the throne, it was temporarily held by the Lord Chief Justice. During the year twenty-two papers were read at the Ordinary Meetings of the Society, six in the Indian, and five in the Colonial Section. The has been, as usual, an increase in the entries for the Society's Examination, the total number of papers worked this year being 34,260. The Society's Albert Medal has been awarded to the Hon. Sir Charles A. Parsons, K.C.B., F.R.S., for his experimental researches into the laws governing the efficient action of steam in engines of the turbine type. The Council, with a few alterations, was re-elected.

Royal Society of Arts' Medals.—The Council of the Royal Society of Arts have awarded Silver Medals for papers read during the past Session as follows:—

At the Ordinary Meetings.—

Campbell P. Ogilvie, "Argentina."
Vaughan Cornish, D.Sc., F.G.S., F.C.S., "The Panama Canal."

Reginald A. Smith, B.A., F.S.A., "Roman London."
Philip Joseph Hartog, M.A., B.Sc., "Examinations."
George A. Stephen, "Bookbinding."
Dr. Leonard Hill, F.R.S., "Caisson Sickness and Compressed Air."

James Cantlie, M.A., M.B., C.M., F.R.C.S., D.P.H., "Plague."

George B. Heming, "Art Education in Jewellery, &c."

Prof. Raoul Pictet, "Les Basses Températures."

Frank M. Andrews, "Architecture in America."

In the Indian Section.—

Robert Fellowes Chisholm, F.R.I.B.A., F.S.A., "The Taj Mahal."

Reginald Murray, "Banking in India."

Claude Hamilton Archer Hill, I.C.S., C.S.I., C.I.E., "Education in India."

Sir Thomas Henry Holland, K.C.I.E., D.Sc., F.R.S., "Mineral Development in India."

W. R. H. Merk, I.C.S., C.S.I., LL.D., "The North-West Frontier Province."

In the Colonial Section.—

A. Montgomery, M.A., F.G.S., "Mining in Western Australia."

F. Douglas Osborne, M.Inst.M.M., "The Tin Resources of the Empire."

Captain R. Muirhead Collins, R.N., C.M.G., "The Commonwealth of Australia."

F. Williams Taylor, "Canadian Banking."

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Northern Lights.—Can any reader give an explanation of the following order of the succession of colours, or of any succession of colours, in what I have usually considered the "northern lights." The colours are golden tint from clouds, blue changing to dark blue, followed by red coloration chiefly from clouds. I have noted these appearances in various parts of England whilst Aurora or rather "northern lights" have been announced in the press.—J. C. T.

THE CHEMICAL NEWS.

VOL. CIV., No. 2694.

SIR ROBERT HADFIELD ON METALLURGY. THE VALUE OF RESEARCH.

THE degree of Doctor of Metallurgy was lately conferred on Sir Robert Hadfield by Sheffield University, and in the course of a speech in connexion with the ceremony he made some interesting remarks on the value of research and other topics.

Sir Robert Hadfield mentioned that his interest in the alloys of iron and steel, the branch of metallurgy to which he had paid special attention, was aroused by the exhibit of the Terre Noire works which he saw at the Paris Exhibition in 1878. It was largely through the researches and efforts of those works that it became possible to produce rich ferro-manganese in the blast furnace, so that instead of costing £90 per ton it could to day be obtained for some £8 to £10 per ton. It was some ten years before his own research bore fruit, manganese steel being one of the first results. His work on that subject, which was put before the Institution of Civil Engineers and the Iron and Steel Institute in 1888 and 1889, he believed was the first presentation of a systematic study with regard to a special element other than carbon added to and alloyed with iron. Faraday conceived the idea of studying iron alloys about 1830, and had an interesting series of them made in Sheffield; but at that time the results were naturally imperfect, and were not carried sufficiently far to be of either practical or scientific value.

In former days most scientific men who were not metallurgists obtained specimens of steel upon which to experiment, and thought that it was quite sufficient to say that their examination had been carried out, for example, upon a bar of carbon steel; even if the carbon percentage was stated, there the *data* usually ended. It was now known, as was shown in his original papers in 1888 and onwards, which described manganese iron or manganese steel, silicon steel, and many other iron alloys, and were followed up by the accurate work done by Dr. Arnold, of the Metallurgical Department of Sheffield University, that there must be complete correlation, including not only composition, but also mechanical tests, micro-structure, complete chemical analysis, and a knowledge of electrical and physical properties. Where the next improvement in the world of iron and steel was to take place was very difficult to say. They wanted, and should probably in due time get, another Bessemer, Siemens, or Sorby. The research work metallurgists undertook represented the great truth of the Chinese proverb that he who held the iron of the world would rule the world. It was not, however, merely holding the iron of the world—China herself did that now, having, he believed, the largest known deposits—but understanding the properties of that metal which would make the masters of the metallurgical world.

The Work of Sheffield University.

To aid in the continuance of metallurgical work there was now the valuable assistance of Sheffield University. It was his firm conviction that Sheffield would not to-day hold the position she did, not merely on the scientific side, but also the commercial, but for the work started in the Applied Science Department of the University years ago by the foresight as well as the liberal financial assistance of, among others, the late Mr. Mark Firth, Sir Frederick Mappin, Sir Henry Stephenson, and Dr. Clifton Sorby, with the wise support of the City Council. If it had not been for the manner in which metallurgical training had been conducted by the University there was no doubt that

more than one erroneous theory, with the attendant evils which sooner or later had to be unlearned, would have arisen. One error which would have now held its sway, to the detriment, at least so it seemed to him, of the true advancement of metallurgical science and knowledge, was the allotropic theory of iron, and the explanation of the hardening of steel as due to the presence of a so-called adamantite β form of iron. Dr. Arnold and his staff had been able by scientific research to show the error of that theory, and to-day Sheffield was to be congratulated upon having been the means of avoiding that pitfall.

Sheffield men could claim to have contributed unselfishly and freely to the world more original research work in the metallurgy of iron and steel than any other section of the Empire, or, in fact, of any other nation. It was no little satisfaction to be able to state this fact when there were still some who always seemed to be thinking that England was taking a back seat and had not kept up with the times. Nothing was further from the truth.

The Value of Research.

Other nations were paying great attention to this question of research. The Reichsanstalt in Germany had done great work, and in Washington the Bureau of Standards was admirably organized and equipped. The National Physical Laboratory in this country was also doing excellent work. Very large sums of money were freely granted, but money was not everything. At the back of it all were the brains which directed the research, and there was no reason why Sheffield should not in the future continue to lead in metallurgical research as she had done in the past.

But her past success must not cause her to rest on her oars. In progressive manufacture the complexity of which increased year by year, there were, in addition to the many ordinary difficulties met with, those of how to solve new problems which constantly presented themselves. This could be done only by research, which should form an actual part of industrial operations, and demanded almost as much attention as was devoted to the manufacturing side. He had recently received from Messrs. Krupp an interesting and most instructive booklet with regard to their new research laboratory, completed at enormous expense and thought. He congratulated them heartily upon their wise expenditure. Nothing was more calculated to keep their works in the prominent position they had occupied in the past. As one who had carried out many researches in metallurgy and had also benefited by the scientific investigation of others, not only in this country, but elsewhere, he could not insist too strongly upon the practical importance of research. It was more than ever necessary not to rest satisfied with the knowledge of to-day, or to think that this would satisfy the needs of to-morrow. Rapid and great changes were constantly occurring in metallurgy as in other branches of scientific knowledge.

Sir James Dewar recently pointed out that the whole cost of a century's research experiments at the Royal Institution, of which he was the able head, had been only about £120,000. What an insignificant sum to pay for the benefits mankind had received from the splendid investigations of Young, Davy, Faraday, Tyndall, Dewar himself, and others! Yet most of their labours were carried out *honoris causa*, not for immediate material benefit.—*The Times*.

New Oxidation of α -Methyl Indol.—G. Plancher and U. Colacicchi.—When α -methyl indol is treated with hydrogen peroxide a product of formula $C_{10}H_{16}N_2O_4$ is obtained, $2C_9H_9H + 2H_2O_2 = C_{18}H_{16}N_2O + 3H_2O$. The reduction of this substance with tin and hydrochloric acid gives benzoyl dihydromethyl indol. Caro's reagent gives rise to the formation of the same oxidation product.—*Atti della Reale Accad. Lincei*, xx., No. 6.

EIGHTH INTERNATIONAL CONGRESS OF
APPLIED CHEMISTRY.

SEPTEMBER 4 TO 13, 1912.

At the instance of the representatives of more than 4000 American chemists, the Congress of the United States by Joint Resolution on March 4, 1909, authorised the President of the United States to invite the Eighth International Congress to meet in the United States. This invitation was extended to the Seventh International Congress in London, June 2, 1909, by the Honourable Whitelaw Reid, Ambassador from the United States to Great Britain, and enthusiastically and unanimously accepted.

The thirteen Delegates sent by the Government of the United States to the Seventh Congress were appointed by that Congress as the nucleus of the Organising Committee for the Eighth Congress, with power to add to their number.

On June 11, 1910, the gentlemen forming this nucleus met and organised for the despatch of business, and at a meeting held August 26, 1910, greatly increased the membership of the Organising Committee. These Official Representatives are primarily charged with the responsibility of seeing to it that none of the interests in their respective jurisdictions are overlooked at the Eighth Congress, and that all are properly represented thereat; they also serve as an official avenue of communication between their respective Governments and the Eighth Congress. This enlarged Organising Committee, on October 8, 1910, provided for a Constitution and By-Laws, and further provided for twenty-five scientific Sections and Sub-sections. One of these—on the leather industries—still remains to be organised if those interested in leather and allied manufacturers desire to have a special Sub-section in the Eighth Congress. Sectional Executive Committees for each of the twenty-four Sections and Sub-sections have been organised. The task of completing the working committees (comprising a total of about twenty-five members each) for all of these twenty-four Sections and Sub-sections is going rapidly forward.

The responsibility for the conduct of the Eighth Congress is vested in the Executive Committee.

The responsibility for the conduct of business before the various Sections and Sub-sections at their sessions during the Congress is vested in a Committee on Sectional Procedure, which Committee is composed of all the Presidents of Sections and Sub-sections, and tentative rules have been framed.

The Committees of Sections and Sub-sections, and particularly their respective Executive Committees, are charged with the responsibility of procuring papers for all their sessions, not only from chemists and others resident in the United States, but also from those resident in all other countries of the world. To the end that the most effective co-operation may be secured, it is earnestly urged that, in all countries outside the United States, there be very soon formed Committees of Sections and Sub-sections corresponding to those established in the United States, or so many of them as will provide fully for the interests of chemists and allied professional and business men in such countries as may not be interested in all the Sections and Sub-sections of the Eighth Congress, and that, upon organisation and announcement of such Committees, all chemists and all chemical and allied societies resident in such country and interested in the Eighth Congress communicate with those of their Committees in whose activities and purposes they are interested, giving the titles and scope of papers or other communications they may contemplate contributing to the Eighth Congress. It is suggested that all such societies within or outside the United States, which desire to co-operate with any particular Section or Sub-section of the Congress, communicate that fact to the President of the corresponding American Sectional Committees. It is further suggested that Chairman of Committees of all Sections and Sub-sections outside

the United States communicate, at stated intervals, preferably the first of every month, to the President of the American Committees of the corresponding Sections or Sub-sections, the titles of papers or other communications promised, together with the names and post office addresses of their authors, so that the American Committee may be able to form an approximate estimate of the probable activities of the respective Sections for the guidance of those responsible for the conduct of the Eighth Congress.

In order that there may be beneficial co-operation and a loose affiliation between the Eighth Congress and its Sections and Sub-sections on the one hand, and other scientific or professional bodies meeting in or near New York or Washington at or about the time of the convening of the Eighth Congress, on the other, a Committee on Co-operation had been established; this Committee will be glad to communicate with any such associations in an endeavour to bring about such co-operation.

The President of the United States has shown his deep interest in the objects and purposes of the Eighth Congress by consenting not only to act as its Patron, but also to preside at the Opening Meeting of the Eighth Congress, which is to be held in Washington, D.C., on Wednesday, September 4, 1912. The President of the United States has also shown his great solicitude for the success of the Eighth Congress by causing invitations to be sent to all the Governments of the World to take part in the deliberations and the work of the Congress. The chemists, individually, and collectively as Societies, not only of the United States, but of all other countries of the world, therefore owe it not only to their science and to their profession to exert every effort to make the Eighth International Congress of Applied Chemistry completely successful, but they also owe it to their own countries and their own Governments to use every means in their power to see to it that every interest in their respective countries is properly and fully represented at the Eighth Congress and to demonstrate to their own Governments and their fellow-countrymen that, in accepting this invitation of the President of the United States, the confidence reposed in the chemists of the respective countries by their Governments has been fully justified. To this end the hearty and enthusiastic co-operation of chemists and allied professional and business men, and particularly of societies of chemists, and of allied professional and business societies the world over, and along the lines suggested at various places in this pamphlet, is most earnestly solicited.

It is hoped that all the matters presented in this pamphlet will be given the widest possible publicity in all chemical and allied societies, and in all chemical and allied publications the world over, and that suggestions for changes which may more surely assist in the realisation of a successful and profitable meeting may be made to the Executive Committee of the Eighth Congress.

Respectfully,

EIGHTH INTERNATIONAL CONGRESS OF APPLIED
CHEMISTRY.

EDWARD W. MORLEY, Honorary President.
WILLIAM H. NICHOLS, President.
BERNARD C. HESSE, Secretary.

The Congress is divided into the following Sections and Sub-sections:—I. Analytical Chemistry. II. Inorganic Chemistry. III.a. Metallurgy and Mining. III.b. Explosives. III.c. Silicate Industries. IV. Organic Chemistry. IV.a. Coal Tar Colours and Dystuffs. V.a. Industry and Chemistry of Sugar. V.b. India Rubber and other Plastics. V.c. Fuels and Asphalt. V.d. Fats, Fatty Oils, and Soap. V.e. Paints, Drying Oils, Varnishes. VI.a. Starch, Cellulose, and Paper. VI.b. Fermentation. VII. Agricultural Chemistry. VII.a. Hygiene. VII.b. Pharmaceutical Chemistry. VII.c. Bromatology and Pharmacology. VII.d. Physiological Chemistry. IX. Photo-Chemistry. X.a. Electro-Chemistry. X.b. Physical Chemistry. XI.a. Law and Legislation affecting Chemical

Industry. XI.b. Political Economy and Conservation of Natural Resources.

Papers will be accepted for reading and discussion in all the above sections, preference being given to those specially adapted for international discussion. They must be sent in not later than July 1, 1912.

A preliminary pamphlet has been issued and may be obtained from the Hon. Secretary of the British Organising Committee, CHARLES G. CRESSWELL, Society of Chemical Industry, Palace Chambers, Westminster, S.W.

IMPROVEMENT OF THE WILEY METHOD FOR DETERMINING THE MELTING-POINTS OF FAT.

By HARRY STEENBOCK.

DURING the course of an extended investigation on the chemical and physical properties of animal fats the writer had occasion to use the Wiley method for determining the melting-point of fats. This exceedingly ingenious method was found difficult of manipulation under all but perfect conditions. However, with a few modifications the operation may be considerably improved.

As is well known to all who have had experience with this method the main difficulty is encountered in securing fat discs perfectly free from occluded air. During the course of the determination, the smallest trace of air is sufficient, by its expansion on heating, to carry the fat disc to the surface of the liquid and thus ruin the determination. With high-melting fats, as tallow, the difficulty is especially great on account of the great change in temperature and therefore great expansion of the air. It is true that the number of air bubbles may be appreciably decreased by preparing the fat discs on ice floating in cold, recently boiled, distilled water. If the water is not near the freezing point, some of the ice will melt and thus introduce air into the water. Some ice used was found to be so full of occluded air that even with these precautions fat discs prepared on it invariably were found to be useless for a melting point determination.

With a view of correcting these difficulties the writer prepared fat disks by dropping the melting fat on cold mercury. By proper adjustment of the height from which the fat is dropped, together with proper control of the temperature of the fat and mercury, discs of very regular shape were obtained. When thoroughly cool and hardened, they were removed with a cold steel spatula and thrown into a beaker containing cold dilute (50 per cent) alcohol. The beaker was then set in a vacuum desiccator and the air exhausted until bubbles ceased to be given off. Usually this was obtained in less than an hour. Discs thus prepared were found to be always free from occluded air and satisfactory in every way for the determination. — *Journal of Industrial and Engineering Chemistry*, ii., Nov. 11.

EIGHTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1910.*

By F. W. CLARKE.

(Continued from p. 6).

Phosphorus.

ATOMIC weight re-determined by Baxter and Jones from analyses of silver phosphate (*Journ. Am. Chem. Soc.*, xxxii., 298).

* *Journal of the American Chemical Society*, xxxiii., No. 3.

Weight Ag_3PO_4 .	Weight 3AgBr .	Ratio
6.02166	8.34490	1.34558
6.35722	8.55419	1.34559
5.80244	7.80819	1.34567
5.05845	6.80685	1.34564
3.34498	3.43544 (AgCl)	0.34560
7.15386	9.62694	1.34570
7.20085	9.68947	1.34560
6.20182	8.34522	1.34561
5.20683	7.00605	1.34555

Mean 1.34562

In experiment 5 the silver was weighed as chloride, but re-calculated to bromide in the ratio. With $\text{Ag} = 107.88$, $\text{P} = 31.043$.

Vanadium.

Prandtl and Bleyer, whose work on the atomic weight of vanadium was noticed in my report for 1909, have published a second memoir on the subject (*Zeit. Anorg. Chem.*, lxxvii., 257). Eight new analyses of vanadyl trichloride are given, of which four are rejected as defective. The four satisfactory determinations follow, with vacuum weights, and the ratio $3\text{AgCl} : \text{VOCl}_3 :: 100 : x$.

Weight VOCl_3 .	Weight 3AgCl .	Ratio
7.77585	19.26836	40.301
8.41904	20.86554	40.311
10.66137	26.42699	40.321
5.53998	13.73492	40.333

Mean 40.3165

From these figures, combined with the earlier series, the authors deduce $V = 51.061$, ± 0.024 , when $\text{Ag} = 107.880$ and $\text{Cl} = 35.460$.

Prandtl and Bleyer also investigated the ratio $\text{V}_2\text{O}_5 : \text{V}_2\text{O}_3$, by reduction of the pentoxide in hydrogen. Their determinations, with vacuum weights, appear in the next table.

Weight V_2O_5 .	Weight V_2O_3 .	At. wt. V.
9.11431	7.51639	51.261
9.85727	8.13127	51.376
8.70923	7.18456	51.395
12.26426	10.11721	51.394

Mean 51.3565 (a)

(a) The authors give 51.374.

Although these determinations agree with Roscoe's, the authors regard them as doubtful. Their VOCl_3 determinations are preferred.

The work of McAdam on this constant consisted in reducing NaVO_3 to NaCl by heating in dry HCl (*Journ. Am. Chem. Soc.*, xxxii., 1603). With vacuum weights, and $\text{NaCl} = 58.46$, the following results were obtained:—

Weight NaVO_3 .	Weight NaCl .	At. wt. V.
4.8564	2.3277	50.966
5.6404	2.7033	50.976
4.4263	2.1220	50.946
5.7805	2.7710	50.952
9.4902	4.5478	50.997

Mean 50.967

Taking into consideration the determinations of Prandtl and Bleyer, the atomic weight of vanadium may be rounded off to 51.

Tantalum.

Balke's determinations of the atomic weight of tantalum are based upon the hydrolysis of the pentachloride (*Journ. Am. Chem. Soc.*, xxxii., 1127). With vacuum weights and $\text{Cl} = 35.46$, the final results are as follows:—

Weight TaCl ₅ .	Weight Ta ₂ O ₅ .	At wt. Ta.
12.99680	8.02326	181.49
9.24957	5.71104	181.60
10.17456	6.28133	181.52
17.99542	11.11014	181.55
11.70558	7.22693	181.55
6.24767	3.85658	181.46
7.26375	4.48398	181.48
15.88270	9.80465	181.49
Mean		181.52

The rounded-off number 181.5 is to be accepted.

Tellurium.

Marckwald and Foizik, by a complex volumetric process, find for this atomic weight the value 127.61 (*Ber.*, xliii., 1710). The data are too bulky and complicated for reproduction here. The purpose of the investigation was not so much to determine the atomic weight exactly, as to ascertain the cause of the low value found in several previous researches.

Flint has continued the work reported by Browning and Flint in 1909 on the fractionation of tellurium by hydrolysis of the tetrachloride (*Am. Journ. Sci.*, [4], xxx., 209). The unfractionated material, by the basic nitrate method, gave $\text{Te} = 127.45$. Progressive diminution of the atomic weight was noted in a series of fractions, namely, the fourth, eighth, and tenth. The tenth gave low atomic weights as shown in the following table:—

Weight Te ₃ HNO ₇ .	Weight TeO ₂ .	At. wt. Te.
2.06311	1.71688	124.25
2.18903	1.82172	124.27
3.56161	2.96446	124.42
2.99821	2.49537	124.37
2.86977	2.38824	124.27
2.47403	2.05898	124.31
4.85363	4.03943	124.32
Mean		124.32

The investigation is still in progress; but the present results are promising, and seem to show that ordinary tellurium is really a mixture. If that should be proved, all former determinations of the atomic weight would go for nothing.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 29th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"On a New Method of Estimating the Aperture of Stomata." By FRANCIS DARWIN, F.R.S., and Miss D. F. M. PERTZ.

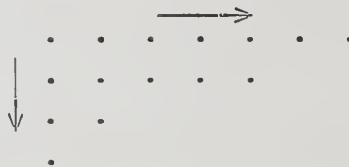
The apparatus here described under the name of *porometer* is similar in principle to that devised in 1873 by N. J. C. Müller, but differs from it completely in construction. By a simple arrangement a current of air is drawn through the stomata of a living leaf, its velocity being measured by the fall of a water-column. At a constant pressure the rate of air-flow is necessarily dependent on the size of the stomatal pores, and it is accordingly found that agencies such as darkness or loss of water-supply, which are known to diminish stomatal aperture, cause a striking drop in the rate of air-flow as recorded by the pyrometer. In studying the effect of severing the leaf stalk and thus cutting off the water-supply, it has been

proved that the first effect of withering is a wide opening of the stomatal pore, confirming F. Darwin, in *Phil. Trans.*, 1898, B, cxc., 548.

The porometer has been found of value in attacking the question of the causal relation between stomatal aperture and transpiration. This subject, on which a large number of observations have been made, will be fully treated elsewhere. In the present paper a single experiment is given illustrating the parallelism between the transpiration rate and the condition of the stomata as revealed by the porometer.

"Memoir on the Theory of the Partitions of Numbers. Part VI. Partitions in Space of Two Dimensions to which is added an Adumbration of the Theory of Partitions in Space of Three Dimensions." By MAJOR P. A. MACMAHON, D.Sc., LL.D., F.R.S.

In this part I consider the partitions of a number, the parts being placed at the nodes of an incomplete lattice in two dimensions. Thus, the lattice being of the nature depicted—



the parts are in descending order of magnitude in each row and in each column. The enumerating generating function is required. It is found that for a lattice of given specification and a given restriction upon the part magnitude the generating function satisfies a functional equation. From this the functional equation satisfied by the corresponding inner-lattice function, as is defined in Part V., is deduced. This investigation then turns upon the determination of the fundamental solutions of this equation and the expression of the generating function by means of them. The complete solution of the problems in hand is thence obtained, and the inner-lattice function is shown to be expressible in an elegant determinant form.

At the end of the paper the subject of three-dimensional partitions is broached. It is shown that the method of lattice functions is again available, and the particular case of partition at the summits of a cube is worked out in detail from this point of view.

The further investigation of this interesting question is reserved for a future communication.

"The Kinetic Theory of a Gas Constituted of Spherically Symmetrical Molecules." By S. CHAPMAN.

This paper may be regarded as a sequel to Maxwell's kinetic theory of a gas whose molecules repel one another according to the famous fifth-power law (*Phil. Trans.*, 1867). Maxwell's deductions from his hypothesis were found not to agree with fact, but the theory was valuable because it was the only mathematically rigorous kinetic theory in existence. When he wrote a later paper on the same subject (*Phil. Trans.*, 1879) he was aware of the defects of his assumption, but was prevented by certain analytical difficulties from generalising his theory by adopting a wider hypothesis.

In this paper these difficulties have been very largely overcome. With the same rigour as in Maxwell's theory, formulæ are deduced for the coefficients of viscosity, diffusion, and thermal conductivity in a simple or compound gas. The molecules are assumed to be spherically symmetrical, but no particular kind of interaction is postulated. The latter, however, is involved in the formulæ by the occurrence, as factors, of two definite integrals.

Certain relations may be deduced without the evaluation of these factors. The most interesting of these is $\delta = \frac{1}{2} \mu C_v$, where δ is the thermal conductivity, μ the viscosity, and C_v the specific heat at constant volume. This formula, which was also obtained by Maxwell, has always

been regarded as a special consequence of his hypothesis, whereas it only depends on the spherical symmetry of the molecules, and is true for rigid-elastic spheres, among other cases.

In general, the formulæ can be completed only by the evaluation of the before-mentioned factors. In the paper this is done for the case of rigid-elastic spherical molecules, for centres of force repelling according to the inverse n -th power law of distance, and for the case of rigid elastic spheres surrounded by fields of attractive force. The last case furnishes a rigorous proof of Sutherland's formula for viscosity, and some important corrections to his theory are made. Finally, the formulæ obtained are compared with experimental results to test the accuracy of the various laws considered, and to obtain improved data concerning the molecules, and other physical constants of gases.

"Radiation in Explosions of Coal-gas and Air." By W. T. DAVID.

"The Mechanical Viscosity of Fluids." By Dr. T. E. STANTON.

The paper deals with the experimental determination of the ratio of the shearing stress to the rate of change of distortion in fluids which are in sinuous or eddying motion. Thus in a fluid in eddying motion flowing through a parallel pipe of circular cross-section, if F is the mean shearing stress on any cylindrical surface of radius r concentric with the pipe, and v the average velocity in the axial direction of the fluid in this surface, then writing $F = \mu' \frac{dv}{dr}$ the object of the experiments was the determination of μ' as a function of the dimensions of the pipe and the velocity of flow. This ratio has been called by Osborne Reynolds "Mechanical Viscosity" to distinguish it from the corresponding ratio when the fluid is in steady or laminar motion, which is the ordinary coefficient of viscosity.

The fluid chosen for the purpose of the experiments was air flowing at speeds up to 2200 cm. per second through pipes 5.08 and 7.35 cms. diameter. A small Pitot tube of width 0.25 mm., connected to a very sensitive gauge, reading to 0.005 mm. of water, has been used for measuring the distribution of velocity, and a second sensitive gauge has been used for the shearing forces. The results of the experiments are as follows:—

1. In pipes artificially roughened so that air friction varied as square of velocity flow, the value of μ' was found to be proportional to the product of speed of flow v_c , and linear dimension of pipe l , i.e., $F = k v_c l \frac{dv}{dr}$ where k is a constant depending on the roughness.
2. In ordinary smooth pipes, the corresponding relation was given by $F = C v_c l \int \left(\frac{V}{v_c l} \right) \frac{dv}{dr}$, where C is a constant and $\int \left(\frac{V}{v_c l} \right)$ a function of the kinematical coefficient of viscosity V and the above product $v_c l$.
3. In ordinary smooth pipes of different diameters, owing to the existence of a region of viscous flow at the boundaries, exact similarity between the distributions of axial velocity from centre to walls only obtains when the two viscosities (μ and μ') are the same for each pipe.

"A Silica Standard of Length." By Dr. G. W. C. KAYE.

The general properties of fused silica, and in particular its remarkably low coefficient of expansion, render this substance specially suitable for the construction of permanent length-standards of the highest class.

The coefficient of expansion of platinum iridium, which has hitherto been the material almost exclusively employed in the best work, is about 9×10^{-6} per degree C., while

that of silica over the ordinary range is about 0.4×10^{-6} , i.e., 1/20 of this amount. It is true that the best qualities of invar, M. Guillaume's nickel-steel containing 36 per cent Ni, have expansion coefficients comparable with that of silica, but experience has shown that while invar is eminently useful for working standards, it is quite unsuitable for primary standards, owing to its large thermal hysteresis. Fused silica, on the contrary, has been found to be practically entirely free from this defect; it enjoys, in the matter of cost, an enormous advantage over platinum-iridium; furthermore, in view of the fact that primary standards are always handled by trained and skilled observers, its comparative fragility is of small consequence.

Modern methods of manufacturing and working silica have rendered it possible to construct a silica line-standard metre. The present model, the first of its kind, consists of a silica tube into which are fused at its ends optically-worked plane parallel slabs of silica. These carry the graduations, and their undersides are platinised. The graduations, defining the metre length, are made by cutting through the platinum film with a ruling diamond. The platinum deposit permits the ruling of very beautiful clean-edged lines.

The bar is supported at the Airy points so that the slabs are horizontal. The lines are viewed from above through the slabs, and are thus seen to advantage.

The apparent length of the standard is independent of any change of tilt of the cover-slips which are used to protect the platinum films. The thickness and position of the end slabs are so arranged that the image of each reference line lies in the "neutral plane" when the bar is immersed in water.

The silica metre was annealed at about 450° C., and shrunk a little over half a micron in the process. It is anticipated that its future secular variation will be negligible so far as practice is concerned.

"The Properties of Oil Emulsions. Part I. Electrical Charge." By RIDSDALE ELLIS, B.Sc.

The electrical charge on the globules and the contact potential at the oil-water interface were obtained from measurements of the migration velocity in an electric field. The apparatus used by Whitney and Blake and by Burton for determining velocity of migration were found not to be accurate, since they did not take into consideration the electrical circulation which takes place, and other factors.

To avoid these errors a microscopic method was employed, and corrections for electrical circulation and other effects were introduced into the method of calculating migration velocity. For determining contact potential in presence of electrolytes it was found necessary to modify the apparatus in order to enable the evolution of gas at the electrodes to be avoided, which would otherwise prevent readings being taken.

It was found that the magnitude of the contact potential at the oil-water interface is of the same order of magnitude for oils of various kinds whether very pure or containing large amounts of impurities. Further, the contact potential at the oil-water interface is of the same order of magnitude as that at the glass-water interface and at the interface between the suspended particles of colloidal metals, lycopodium, quartz, and other substances. From these and other considerations it would appear that the contact potential in neutral solution depends almost wholly on the dielectric constants of the suspended particle and of the medium in which it is suspended.

The contact potential at the oil-water and glass-water interface is a maximum in neutral or slightly alkaline solutions. Thus the addition of caustic soda at first increases the contact potential at the oil-water interface, but when the concentration exceeds 0.001 N the contact potential is diminished, rapidly at first, and then slowly. In the glass-water interface the maximum potential appears to be in neutral solution. If hydrochloric acid is added the contact potential is reduced very rapidly for small concentrations, but only slowly for comparatively high concentrations.

"On a Class of Parametric Integrals and their Application in the Theory of Fourier Series." By Dr. W. H. YOUNG, F.R.S.

In this paper the following theorem, *inter alia*, is proved:—

If $(f)x$ and $g(x)$ are two functions whose $(1 + \frac{1}{p})$ th power and $(1 + \frac{1}{p})$ th power respectively are summable, and if $(a_n, b_n), (a_n, \beta_n)$ be their Fourier constants, then the series whose general term is $(a_n a_n + b_n \beta_n) \cos n\theta$ is the Fourier series of a continuous function, a simple expression for which is given.

From this theorem follows as a corollary that if the series—

$$\frac{1}{2} a_0 a_0 + \sum_{n=1}^{\infty} (a_n a_n + b_n \beta_n)$$

converges it has—

$$\frac{1}{\pi} \int_{-\pi}^{\pi} f(x) g(x) dx$$

for its sum, and more generally it always has this expression for sum when the summation is performed in the Cesaro manner.

The method employed is shown also to lead to results of analogous nature, previously known. It involves the study of certain parametric integrals and of a theorem in the theory of sets of points stated and proved in the paper, to the effect that if a set of points of positive content be shifted bodily a sufficiently small distance along the straight line on which it is situated, it necessarily coincides with its original position as to a sub-set of points whose content may be made as near as we please to the content of the set.

"Mode of Generating Fourier Series." By Dr. W. H. YOUNG, F.R.S.

"Pendulum Clocks and their Errors." By H. R. A. MALLOCK, F.R.S.

The errors to which pendulum clocks are liable may be divided into three classes, viz.:—

1. Those which may affect free pendulums oscillating in *vacuo*.
2. Errors depending on the action of the air or gas in which the oscillation takes place.
3. Errors due to the escapement and maintaining mechanism.

In good clocks, unexplained variations of rate are not uncommon, and may be as large as half a second a day, or even more. At any rate, a clock whose rate continues constant within 1/200,000 for a year or more is exceptional, and anything which succeeds in securing a constancy of rate better than 5 parts in a million may be considered an improvement.

In discussing the various sources of change of rate, all matters (as far as the author knows) which can alter the period by as much as 10⁻⁸ are taken into account. It appears that most of the anomalous changes of rate are due to variation of friction in the escapement and maintaining mechanism, which acts chiefly, but not exclusively, by altering the arc of vibration. A graphic method is given for determining in detail the action of escapements on the period.

"Ceratophora, the Type of a New Family of Alcyonaria." By Prof. SYDNEY J. HICKSON, F.R.S.

"Sensibility of the Eye to Variations of Wave-Length." By W. WATSON, D.Sc., F.R.S.

The author has compared the width of Edridge Green's monochromatic patch with the minimum change in wavelength perceptible as a change in hue in the yellow under exactly similar conditions, and finds there is a marked difference. It is also shown that an admixture of white light would not account for the increased sensitiveness when two monochromatic patches are compared.

"Distribution of Slide in a Right Six-face Subject to Pure Shear." By E. N. DE C. ANDRADE.

"Viability of Human Carcinoma in Animals." By Major C. L. WILLIAMS, M.D.

"Structure and Physiological Significance of the Root-nodes of *Myrica gale*." By Prof. W. B. BOTTOMLEY.

"Surface Electric Charges of Living Cells." By H. W. HARVEY and W. B. HARDY, F.R.S.

"Reflex Inhibition of the Knee Flexor." By Prof. C. S. SHERRINGTON, F.R.S., and Miss S. C. M. SOWTON.

"Origin of Osmotic Effects. IV. Note on the Differentia Septa in Plants with Reference to the Translocation Nutritive Materials." By Prof. H. E. ARMSTRONG, F.R.S., and Dr. E. F. ARMSTRONG.

CHEMICAL SOCIETY.

Ordinary Meeting, June 15th, 1911.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

MESSRS. William Gidley Emmett, J. T. M. Dunlop, and A. W. Titherley were formally admitted Fellows of the Society.

The PRESIDENT stated that the Council, at their meeting held that afternoon, had sealed an Address of Congratulation to His Majesty King George V. on the occasion of his Coronation, and an Address of Congratulation to the University of St. Andrews on the Celebration of the Five Hundredth Anniversary of the Foundation of that University.

To His Most Gracious Majesty King George V.

MAY IT PLEASE YOUR MAJESTY.—We, the President, Council, and Fellows of the Chemical Society beg leave to offer to your Majesty our sincere and most respectful congratulations on the auspicious event of your Coronation.

We approach you with the more confidence when we remember how much the science of Chemistry and the position of our Society are indebted to the favours of your august House. We ever bear in mind that a Royal Charter was granted to the Chemical Society by Queen Victoria, and that the Royal College of Chemistry, which was so largely instrumental in fostering and developing the study of our science in this country, was founded by your illustrious Grandfather, the late Prince Consort. It is, moreover, with special gratitude that we recall the lively interest which, as recently as two years ago, was taken by your Majesty and her Majesty Queen Mary in the International Congress of Applied Chemistry, when you extended the Royal welcome to the chemists of all nations assembled in the Capital.

We venture to hope that not only chemical research, but the pursuit of all useful knowledge, may be promoted and furthered in this realm under your benevolent and gracious patronage, and we beg to assure your Majesty of our loyal devotion as we do earnestly hope and pray that your Majesty's reign may be long, happy, and fruitful.—Signed on behalf of the Chemical Society,

(Signed) PERCY F. FRANKLAND, President.
ALEXANDER SCOTT, Treasurer.
ARTHUR W. CROSSLEY, } Honorary
G. T. MORGAN, } Secretaries.
HORACE T. BROWN, Foreign Secretary.

Dated this the Fifteenth Day of June, One Thousand Nine Hundred and Eleven.

To the University of St. Andrews.

On the auspicious event of the Celebration of the Five Hundredth Anniversary of the Foundation of your University, we, on behalf of the Chemical Society, desire to offer you our most sincere and hearty congratulations.

We share the world-wide interest which is evoked by the oldest and most picturesque of the Scottish Universities, and we rejoice to think that this ancient seat of knowledge should have so early recognised the claims of natural science as to establish a Chair of Chemistry already one hundred years ago.

We congratulate you on your not having allowed the venerable traditions of the past to overshadow the urgent needs of the present, and we cordially admire the munificent and devoted generosity of your friends in raising the worthy buildings, equipped on modern lines, for the study of Chemistry.

It is, moreover, with lively satisfaction that we have come to regard your Chemical School as an active and fertile centre of research, in which have been conducted a large number of valuable investigations, the results of which are embodied in the *Transactions* of our Society.

We trust that the now happily accomplished absorption of the Dundee College by the University may prove of great mutual benefit, and that the blending of the young institution with the old may be a guarantee of continued strength and fertility.

In the name of the Council and Fellows of the Chemical Society we wish you all prosperity in the future, and we would express the earnest hope that the grey Town set by the Northern Sea may never cease to attract and inspire active workers, not only in our own science, but also in other branches of learning.—Signed on behalf of the Chemical Society,

(Signed) PERCY F. FRANKLAND, President.
ALEXANDER SCOTT, Treasurer.
ARTHUR W. CROSSLEY, } Honorary
G. T. MORGAN, } Secretaries.
HORACE T. BROWN, Foreign Secretary.

Dated this the Fifteenth Day of June, One Thousand Nine Hundred and Eleven.

The PRESIDENT announced that the Secretary of State had intimated his intention of making regulations dealing with the smelting of materials containing lead, the manufacture of red- or orange-lead, and the manufacture of flaked litharge, in accordance with a draft, copies of which may be obtained on application to the Factory Department, Home Office, London.

Certificates were read for the first time in favour of Messrs. Lionel Gowing-Scopes, 3, Estcourt Street, Devizes; George Wishart, B.A., Royal School, Armagh.

A ballot for the election of Fellows was held, and the following were declared subsequently duly elected:—Ernest Andrew Atkins; Norman Ernest Atkinson; Arthur Owen Blackhurst; George Arthur Bradshaw, M.Sc.; Arthur Frederick Clarke; Charles Ernest Cooke; Thomas Cowling; Ganesh Datta, B.A.; Rudolph Demuth; Benjamin Galloworthy; Edgar Harold Gardner; Jages Chandra Ghose, M.A.; Cyril Herbert Kiszelski Gonnville; Rowland Lewis Gould; Edward Lionel Joseph; Henry Edmund Linenbröcker; Herbert James Ling; Richard William Merriman, M.A.; Felix Gabriel Paul; Leonard Ison Pitt, B.Sc.; William Keighley Walton.

Of the following papers, those marked * were read:—

*174. "The Alleged Complexity of Tellurium." By AUGUSTUS GEORGE VERNON HARCOURT and HERBERT BRERETON BAKER.

It has been asserted by Flint (*Am. Journ. Sci.*, 1910, [4], xxx., 209) that tellurium can be separated into two fractions by partial precipitation of the tetrachloride by water.

Using 200 grms. of highly purified telluric acid, the authors have repeated the work. After four partial precipitations, Flint obtained a diminution of a whole unit in the atomic weight of tellurium, but the authors find that the atomic weight is not altered. The mean result of five determinations of the atomic weight of the fourth fractionation was 127.54, that of material similarly purified, but without the fractional precipitation, being 127.53. They

conclude that no separation is effected by this method, and that it is probable that Flint's material was insufficiently purified.

DISCUSSION.

Prof. ERNST COHEN said that he was extremely interested in the facts communicated by Dr. Baker, as they cleared up several doubtful points in some researches on the allotropy of tellurium which had been carried out during the last two years in his (the speaker's) laboratory.

It had been known for a long time that allotropic forms of tellurium existed, but we have been entirely ignorant of the relations between them and of the conditions under which they could be formed. The measurements of Exner, Berthelot, Beljankin, and others in this direction, did not agree with each other, but an explanation of this disagreement was found in the fact that the allotropic change of one of these forms was markedly affected by light, which displaced the equilibrium.

Flint's recent statements introduced difficulties which the authors had now removed, as they had shown that tellurium must still be regarded as a single elementary substance. It was thus possible to bring all these phenomena, which appeared so mysterious, under the head of dynamical allotropy.

*175. "The Purification and Properties of Acetic Acid." By WILLIAM ROBERT BOUSFIELD and THOMAS MARTIN LOWRY.

Acetic acid may be purified by distilling from potassium permanganate, using a still-head to retain acids of higher boiling-point, and then freezing to remove the water. The purified acid melts at 16.60°, and has a density of 1.05148 at 18°/4°, and 1.04922 at 20°/4°; its maximum conductivity when mixed with water is $\kappa_{18} = 0.0016415$.

DISCUSSION.

Dr. VELEY remarked that those workers who had been engaged in the purification of even the commonest acids could fully appreciate the difficulties encountered in preparing acetic acid free from its homologues, so as to obtain trustworthy data for its physical constants, such as electrical conductivity, melting-point, and density.

The method adopted for destroying the formic acid by oxidation with potassium permanganate appeared to be of especial interest, as doubts had been expressed as to the statements contained in text-books that formic acid can be completely oxidised under these conditions.

Dr. WADE said that in purifying acetic acid for the preparation of esters he had succeeded in eliminating propionic acid and its immediate homologues by fractional distillation with a small quantity of water, with which it was perhaps not generally known that all the lower fatty acids, with the exception of acetic acid, formed volatile azeotropic mixtures. He employed, however, an evaporator still-head, which, as Young had shown (*Trans.*, 1899, lxxv., 699), was much more efficient than the pear column employed by the authors. He doubted whether the oxidisable impurity observed by the authors was formic acid; it was well known that other oxidisable impurities were often present in commercial acetic acid.

Dr. L. F. GUTTMANN stated that in the course of some experimental work on mixtures of acetic acid and acetic anhydride he had had occasion to prepare pure acetic acid.

On attempting to do so by freezing a large quantity of "purest" glacial acetic acid, allowing it to thaw partially, discarding the liquid portions, and repeating this procedure five or six times, he had expected to obtain a glacial acetic acid of a high degree of purity; the analysis of this acid, however, gave over 100 per cent.

The normal solutions used were most carefully standardised, yet the result remained the same. Pure acetic acid, giving a value of 100 per cent, was subsequently obtained by fractional distillation of the products; it therefore appeared as if pure commercial acetic acid might contain some acetic anhydride which could not be removed by fractional crystallisation.

He wished to know whether the authors had had similar experiences.

Dr. TITHERLEY pointed out that the reducing substance supposed to be formic acid might be glyoxylic acid, which was a common impurity in acetic acid, and which would probably pass over in the earlier fractions on distillation. As glyoxylic acid in small quantities would account for the observations of the authors, he asked if any attempts had been made to prove the presence or absence of this substance.

Dr. LOWRY, in reply, said that the acetic acid was distilled in presence of a little water, but the quantity was not sufficient to carry over the higher homologues before the acetic acid as a minimum boiling mixture.

The permanganate method of purification had the advantage that there was no real risk of producing any acetic anhydride; the acid was distilled while still moist, and was subsequently dried by freezing.

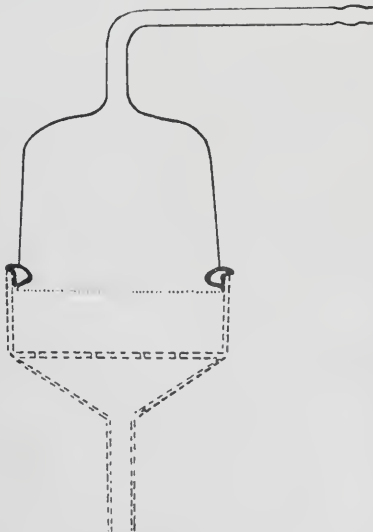
The oxidisable impurity of low boiling-point might contain glyoxylic acid, but the object was to get rid of it, and not to identify or isolate it.

*176. "The Solubility of Carbon Dioxide in Beer." By ALEXANDER FINDLAY and BUCCHOK SHEN.

Previous experiments on the absorption of carbon dioxide by beer (Langer and Schultze, *Zeit. für das ges. Brauwesen*, 1879, ii., 369) have been interpreted as showing that beer dissolves more carbon dioxide than the corresponding water-alcohol solution; and the supposed increase has been attributed to adsorption by the colloids present in beer (Emslander and Freundlich, *Zeit. Phys. Chem.*, 1904, xlix., 317). These conclusions, however, are not in harmony with experiments carried out by Findlay and Creighton (*Trans.*, 1910, xcvi., 536), and the authors now show that carbon dioxide is, as a matter of fact, less soluble in beer than in the corresponding water-alcohol solution, and that the contrary conclusion reached by Langer and Schultze must be attributed to their having used beer supersaturated with carbon dioxide.

*177. "An Addition to the Buchner Funnel." By ALFRED CHARLES GLYN EGERTON.

The apparatus consists simply of a small glass hood, which can be connected to a drying tube. The glass hood is made of such a diameter that it fits inside a Buchner funnel, the joint being made air-tight with a rubber ring



situated in a groove round the rim of the hood. It is well to employ a gentle pressure with the ring of a retort-stand to hold the hood in position, unless working with air under diminished pressure. A precipitate collected in the usual

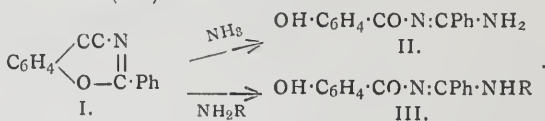
manner on the funnel can be dried by means of this simple additional apparatus in a very short time. Besides dispensing with the trouble of transferring the precipitate to a desiccator, the apparatus saves much time in the drying. The drying is most rapid when a steady, not too rapid, stream of air is drawn through the apparatus by means of the filter pump after passing through a large drying tower filled with calcium chloride; further, the hood, which is made of blown glass or, for very rapid drying, of metal, can be warmed with a flame. The precipitate can, if desired, be dried under diminished pressure by affixing a screw clip to the air inlet of the drying tower. Another application of the apparatus is the drying of a precipitate in a non-reactive atmosphere; the gas can be circulated round and round, if necessary, by means of a blowing arrangement fitted to the filter-pump.

This small inexpensive apparatus changes a Buchner funnel into an exceptionally efficient desiccator, which dries, not only precipitates collected on the funnel by the usual methods employed therewith, but also can be used conveniently for drying crucibles, &c., in a current of dry air.

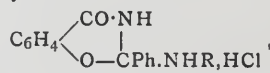
(We are indebted to the Chemical Society for permission to reproduce the accompanying illustration.)

*178. "The Action of Ammonia and Amines on 2-Phenyl 1:3-benzoxazine-4-one." By ARTHUR WALSH TITHERLEY and ERNEST CHISLETT HUGHES.

2-Phenyl-1:3-benzoxazine-4-one (I.) readily combines with ammonia, giving bright orange needles of salicylbenzamidine (II.), and primary amines, giving yellow derivatives (III.) of similar constitution:—



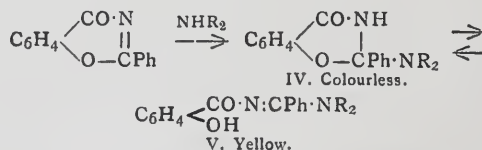
These amidine derivatives give colourless hydrochlorides possessing the cyclic constitution:—



which are very unstable, and readily lose ammonia or an amine, passing through the cyclic compound I. into N-benzoylsalicylamide in presence of water. The free cyclic bases, which are intermediate compounds in the synthesis of the amidines II. and III., are too unstable to exist in the free state.

Salicylbenzamidine (II.) may also be synthesised from phenyl salicylate and benzamidine, and o-hydroxytriphenylcyanidine also results as a secondary product.

2-Phenyl-1:3-benzoxazine-4-one combines with secondary amines, giving mixtures of labile isomeric cyclic and open-chain compounds of the type IV. and V.:—

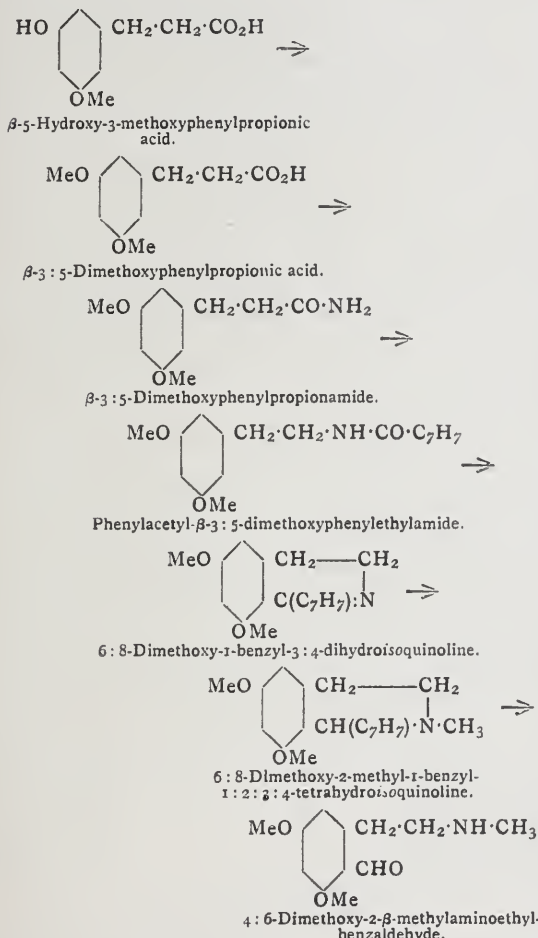


With dimethylamine no proper separation could be effected, but with diethylamine the colourless compound (IV.) was isolated. With diphenylamine a bright yellow compound (V.) was obtained, which, owing to steric influences, does not possess normal phenolic properties. It is probable that in all the yellow open-chain derivatives the molecule is bordering on ring-formation, and the colour is attributed to the disturbance of residual affinity thus created. Replacement of the hydrogen atom of the phenolic hydroxyl group by methyl in salicylbenzamidine leads to a colourless compound, the velocity of hydrolysis of which is normal as compared with similar amidines,

whilst that of salicylbenzamidine and its derivatives is abnormally high owing to ring-formation.

*179. "Synthesis of 4:6-Dimethoxy-2-β-methylaminoethylbenzaldehyde." By ARTHUR HENRY SALWAY.

4:6-Dimethoxy-2-β-methylaminoethylbenzaldehyde has been synthesised from β-5-hydroxy-3-methoxyphenylethylamine (*Trans.*, 1910, xcvi., 2413) according to a series of reactions similar to those employed by the author in the synthesis of cotarnine (*Trans.*, 1910, xcvi., 1208). The stages involved in this process are represented by the following scheme:—



4:6-Dimethoxy-2-β-methylaminoethylbenzaldehyde closely resembles cotarnine in its physiological action on the isolated uterus. On the other hand, it is considerably less toxic than the latter compound.

DISCUSSION.

Dr. TITHERLEY inquired whether the author had instituted any experiments to determine which of the alternative tautomeric (open-chain or cyclic) formulæ represented the constitution of cotarnine and allied derivatives.

180. "Cupriglycollates." By SPENCER UMFREVILLE PICKERING.

That the cupri-compounds formed by the action of alkalis on copper salts contain their copper in the form of CuO or CuOH, and not as metal displacing hydrogen atoms, has been shown by determinations of the molecular weights of six such compounds (*Trans.*, 1911, xcix., 169); more conclusive evidence has now been obtained by finding

that in potassium cupriglycollate the ratio of Cu : K is 1 : 1, in accordance with the formula CH₂O(CuOH)·CO₂K, and not 1 : 2, as it would have to be if the metal displaced hydrogen: (CH₂O)₂Cu(CO₂K)₂.

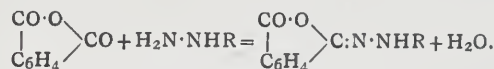
From a solution of copper glycollate mixed with excess of potassium hydroxide, alcohol precipitates a mauve-coloured, strongly alkaline crystalline substance, which agrees in composition and properties with the γ-cupri-salts (containing the cuprite group) suggested as existing in such solutions. The corresponding salts of sodium and rubidium (probably, also, of barium) have been obtained, but not those of lithium, caesium, or calcium. On heating, they seem, in some cases, to be transformed into compounds in which an atom of copper displaces two atoms of hydrogen in alcoholic hydroxyl groups.

181. "Polymorphic Phthalylhydrazides." By FREDERICK DANIEL CHATTAWAY and DONALD FREDERICK SANDYS WÜNSCH.

Some years ago it was observed that phthalylphenylhydrazide, when crystallised from any ordinary solvent, separates almost invariably in two modifications different both in crystalline form and in colour. Each modification could be obtained free from the other by altering the temperature at which crystallisation took place. While this work was in progress, Dunlap (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1091) published an account of similar observations, and it was consequently discontinued.

The authors have recently again investigated the subject to ascertain if this property of crystallising in two forms is common to all phthalylhydrazides. So far, only one other instance has been found among the simple phthalyl derivatives studied, but it seems certain that this is due to the exact conditions necessary for the appearance of the second modification not having been realised, many other observations on related compounds, which will be communicated later, leading to the conclusion that it should be possible to obtain every phthalyl and substituted phthalyl hydrazide in two forms.

A large number of phthalylhydrazides were described. These compounds are very easily obtained by heating together phthalic anhydride and the corresponding hydrazine; the reaction which occurs may be formulated thus:—



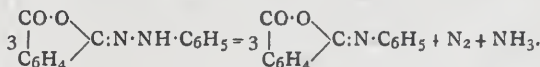
The crystals separating at the higher temperature are bright yellow or orange, those into which they pass when the temperature is lowered being almost colourless.

In every case where only one modification has been observed, it is the one having the deep orange colour.

182. "Decomposition of Hydrazides and Hydrazones by Heat." By FREDERICK DANIEL CHATTAWAY, CHARLES LINAUS CUMMING, and BERNARD HOWELL WILSDON.

In continuation of an investigation into the action of heat on hydrazides, the reactions which take place when various hydrazides and hydrazones are heated have been studied.

When the phthalylhydrazides are heated, vigorous reaction, accompanied by the evolution of heat, sets in at a definite temperature, nitrogen and ammonia are liberated, and a phthalanil is produced; for example:—



In the case of hydrazones two main reactions take place, resulting in the formation of an unsaturated hydrocarbon, nitrogen, and a saturated hydrocarbon; thus, for example:—



or in the formation of an aldehyde-anilide, nitrogen, and ammonia, thus—

$3\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5 = 3\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_5 + \text{N}_2 + \text{NH}_3$, a somewhat larger amount of the hydrazone, as a rule, undergoing the latter decomposition. It seems highly probable that the so-called β -phthalylphenylhydrazide, melting at 210° , is really impure phthalanil produced from the ordinary α or phthalylphenylhydrazide by the above-described decomposition.

183. "Some Reactions of Gum Kino." By JOHN LIONEL SIMONSEN.

The author described some experiments on the constituents of the gum of *Pterocarpus Marsupium*.

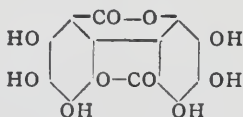
184. "Electromotive Forces in Alcohol. Part I. Concentration Cells with Electrodes Reversible to Chlorine Ions." By ARTHUR LAPWORTH and JAMES RIDDICK PARTINGTON.

Fairly satisfactory results may be obtained with such cells, containing alcoholic hydrogen chloride, with electrodes of silver or mercury, and with silver chloride and mercurous chloride, respectively, as depolarisers.

The transport number of chloridion is found to be about 0.37, as contrasted with 0.16 in aqueous hydrochloric acid. It was shown that this is due to the hydrogen ion, as the transport numbers for the ions of most salts hitherto examined do not appear to be greatly affected by such a change of solvent.

185. "Some Oxidation Products of the Hydroxybenzoic Acids." Part III. By ARTHUR GEORGE PERKIN.

The substance $\text{C}_{14}\text{H}_{10}\text{O}_{10}$, now termed *caeruleoellagic acid*, previously obtained by heating ellagic or flavellagic acid with sulphuric acid (*Proc.*, 1906, xxii., 114), can also be prepared by the action of arsenic acid on the sulphuric acid solutions of these compounds. The acetyl derivative $\text{C}_{14}\text{H}_{10}(\text{C}_2\text{H}_3\text{O})_6$ melts at $330-332^\circ$, and is in reality colourless, and the benzoyl compound $\text{C}_{14}\text{H}_{10}(\text{C}_7\text{H}_5\text{O})_6$ forms needles melting at $343-345^\circ$. By distillation with zinc dust, caeruleoellagic acid gives fluorene, and with boiling potassium hydroxide solution a substance $\text{C}_{12}\text{H}_{10}\text{O}_8$, which crystallises in prismatic needles, and is evidently an *octahydroxydiphenyl* the acetyl derivative of which, $\text{C}_{12}\text{H}_2\text{O}_8(\text{C}_2\text{H}_3\text{O})_8$, forms colourless needles, melting at $177-178^\circ$. Caeruleoellagic acid, to which the constitution:—



is assigned, dyes mordanted fabrics similarly to flavellagic acid, but somewhat more strongly.

186. "The Triazo-group. Part XIX. Nitrosoazides of Dibentene, d-Limonene, and l-Limonene." By MARTIN ONSLOW FORSTER and FREDERIK MARINUS VAN GELDEREN.

Dipentene nitrosoazide, $\text{C}_{10}\text{H}_{15}(\text{NOH})\cdot\text{N}_3$, prepared from either the nitroschloride or the nitrosate by the action of sodium azide in aqueous alcohol, crystallises from methyl alcohol in colourless plates, melting at $72-73^\circ$; alcoholic potash eliminates hydrazoic acid, producing *i*-carboxime. *i*-Triazodihydrocarvone, $\text{C}_{10}\text{H}_{15}\text{ON}_3$, arising from the foregoing nitrosoazide (its oxime) by the action of hot aqueous oxalic acid, is a colourless liquid, having a pleasant odour of peppermint; it boils at $81^\circ/0.4$ mm., and has $D_{1.0409/20^\circ}$. The *semicarbazone* melts at $132-133^\circ$.

d-Limonene nitrosoazide, $\text{C}_{10}\text{H}_{15}(\text{NOH})\cdot\text{N}_3$, whether prepared from the α - or the β -nitroschloride, melts at $52-53^\circ$, has $[\alpha]_D 6.5^\circ$, and is converted into *l*-carboxime by the action of alcoholic potash. *d*-Triazodihydrocarvone, $\text{C}_{10}\text{H}_{15}\text{ON}_3$, produced when the nitrosoazide is heated with aqueous oxalic acid, boils at $93^\circ/0.46$ mm., has $D_{1.0487/20^\circ}$ and $[\alpha]_D 88.49^\circ$; the *semicarbazone* melts at 220° .

l-Limonene nitrosoazide, $\text{C}_{10}\text{H}_{15}(\text{NOH})\cdot\text{N}_3$, melting at $52-53^\circ$, and having $[\alpha]_D -3^\circ$, gives *d*-carboxime with alcoholic potash. *l*-Triazodihydrocarvone, $\text{C}_{10}\text{H}_{15}\text{ON}_3$, obtained by hydrolysis with oxalic acid, boils at $93-94^\circ/0.48$ mm., has $D_{1.0472/20^\circ}$, and $[\alpha]_D -92.5^\circ$; the *semicarbazone* melts at 220° .

187. "The Relation of the Velocity of Chlorination of Aromatic Compounds to Constitution. Part I. Chlorination of Anilides." By KENNEDY JOSEPH PREVITÉ ORTON and HAROLD KING.

The speed of chlorination (formation of monochloro-derivatives) of a number of acylanilides has been measured in glacial acetic acid solution. It was shown that the rate of the reaction varies enormously with the character of the substituent in the benzene nucleus. The nature of the acyl groups has a comparatively subsidiary effect.

Naphthalides are chlorinated at a far greater rate than the anilides.

188. "Chlorination of Acylanilides. Effect of the Constitution of the Acyl Group on the Proportion of the Ortho- and Para-derivatives." By HAROLD KING and KENNEDY JOSEPH PREVITÉ ORTON.

The proportion of *o*- and *p*-chloro-derivatives produced in the chlorination of form-, propion-, stear-, and benz-anilide has been estimated. Comparison with acetanilide (Jones and Orton, *Trans.*, 1909, xcv., 1056) shows that the largest proportion of the *o*-chloro derivative is formed in this case. Acetanilide yields 45, propionanilide 26, stearanilide 12, benzanilide 11, and formanilide 3 per cent of the *o*-chloro-derivative.

189. "The Influence of the Alternating Factor in certain Series on the Molecular Volumes at the Melting-point." By GERVAISE LE BAS.

An examination of the molecular volumes of the paraffins at the melting-point shows that the volume differences for CH_2 alternate in value exactly as do the melting-points in several homologous series.

By finding the number of H equivalents in each compound (since $\text{C} = 4\text{H}$), that is, W , and dividing this into the volume at the melting-point, V , the ratio V/W gives the volume of H in each compound.

The molecular volumes of the normal paraffins at various temperatures can be calculated by means of interpolation formulæ with two constants.

I.—Table of Constants.

Compound.	M.W.	W.	M.P.	d_x .
Nonane, C_9H_{20} ..	128	56	-51.0°	$0.7330 (0^\circ)$
Decane, $\text{C}_{10}\text{H}_{22}$..	142	62	-32.0°	$0.7454 (0^\circ)$
Undecane, $\text{C}_{11}\text{H}_{24}$..	156	68	-26.5°	$0.7557 (0^\circ)$
Dodecane, $\text{C}_{12}\text{H}_{26}$..	170	74	-12.0°	$0.7730 (\text{m. p.})$
Tridecane, $\text{C}_{13}\text{H}_{28}$..	184	80	-6.2°	$0.7755 (\text{m. p.})$

II.—Constitutive Effects in the Volumes of Compounds at the Melting-points.

Compound.	W.	M.V.	Δ .	Δ between—		V/W (odd).	V/W (even).
				Odd No.'s.	Even No.'s.		
C_9H_{20} ..	56	165.67	18.9	35.7	—	2.957	—
$\text{C}_{10}\text{H}_{22}$..	62	184.54	16.9				
$\text{C}_{11}\text{H}_{24}$..	68	201.4	18.5	35.9	—	2.962	—
$\text{C}_{12}\text{H}_{26}$..	74	219.9	17.4				
$\text{C}_{13}\text{H}_{28}$..	80	237.3	18.1	35.9	—	2.966	—
$\text{C}_{14}\text{H}_{30}$..	86	255.4	17.8				
$\text{C}_{15}\text{H}_{32}$..	92	273.2	18.0	53.8	—	2.970	—
$\text{C}_{16}\text{H}_{34}$..	98	291.2	17.8				
$\text{C}_{17}\text{H}_{36}$..	104	309.0				2.971	

Study of the data shows that:—

1. The even members of the series show augmented values of V/W, and the odd members depressed values. This is in accord with the fact that the melting-point curves are different, the one for the odd members falling below that for the even members.

2. The values of V/W for the even members diminish to a constant value, 2.970, and those for the odd members increase to the same constant value. Thus, again, there is correspondence between the melting-point and volume curves in that the double curves gradually approach each other as the series is ascended.

The conclusion is drawn that for both the volumes and the melting-points the alternating factor always exerts a depressing effect on the compound with an odd number of carbon atoms, and an elevating one on the compound with an even number of carbon atoms. The alternating factor consequently similarly affects both physical properties.

190. "The Elimination of Bromine from Phenyl *p*-Methoxystyryl Ketone Dibromide." By FORSYTH JAMES WILSON and ALFRED ARCHIBALD BOON.

The authors find that when phenyl *p*-methoxystyryl ketone dibromide is treated with propyl alcohol, isobutyl alcohol, benzyl alcohol, or acetic acid, one of the products is phenyl bromo-*p*-methoxystyryl ketone, $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CBr} \cdot \text{CH} \cdot \text{COPh}$ or $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CBr} \cdot \text{COPh}$, which melts at 93–94°.

When the dibromide is heated with isopropyl alcohol, *tert*-butyl alcohol, acetone, or benzoin, the ketone is regenerated.

191. "Some New Inorganic Salts." By THOMAS VIPOND BARKER. (This paper was communicated at the meeting on June 1st).

In continuation of previous work on the regular growths on each other of isomorphous crystals, the author has completed the investigation of the series of alkaline periodates by the inclusion of the lithium salt, which proves to be entirely different from the compound described (but not analysed) by Rammelsberg, so that it seems probable that his compound was an impure specimen of sodium periodate.

A further contribution to the list of isomorphous substances has been made by the preparation of two new double chromates of the general formula $\text{R}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, in which R = Rb or Cs; these two salts prove to be strictly isomorphous with the corresponding ammonium salt prepared some sixty years ago by Murmann, and with the better known series of double sulphates.

FARADAY SOCIETY.

Ordinary Meeting, June 13th, 1911.

Mr. G. T. BEILBY, F.R.S., in the Chair.

PROF. ERNST COHEN, of the University of Utrecht, delivered a lecture on "Allotropic Forms of Metals." The lecture was illustrated by experiments and lantern slides.

The property of a chemical element to occur in different modifications is called allotropy, a word introduced into chemistry by Berzelius in 1841.

Only a few elements were presumed to show allotropy, but the researches of the last few years make it probable that all elements show it. We have to seek for the conditions which enable them to take different forms. The lecturer pointed out that the conceptions which the physical chemistry of the last quarter of a century has brought us enable us to bring allotropy under the head of equilibrium phenomena.

He discussed enantiotropy, monotropy, and dynamical allotropy, and outlined the results of some of the investi-

gations carried out in these directions by himself and his collaborators, Professor Katsuji Inouye and Drs. Collins, van Eyk, Goldschmidt, Kröner, Olie and Strengers, during the last twelve years.

As a striking illustration of enantiotropy, he referred to the transformation of tin into a grey form (*tinpest*), a phenomenon that has great importance for the technical use of this metal, seeing that the transition point between the white and grey forms is at 18° C., and that below that temperature all ordinary tin is in a metastable condition. Some striking examples of the gradual transformation that had taken place in old tin vessels were exhibited, and the phenomenon of "infection" was likewise discussed.

Monotropy was illustrated by the consideration of "explosive antimony," a mysterious form of antimony discovered in 1854 by Dr. Gore, of Birmingham, and prepared by electrodeposition from the haloid solutions of the metal. Unlike in the case of tin, there is here no transition equilibrium temperature; at every temperature the metastable form of antimony changes to the stable form, becoming therefore less and less explosive as time goes on.

As typical cases of dynamic allotropy white and violet phosphorus, as well as tellurium, were cited, although the researches on the latter element are still going on in the lecturer's laboratory.

Prof. J. A. EWING asked whether there was any connection between the slow process of re-crystallisation that went on in metals after strain and the phenomena described in the lecture.

Dr. W. ROSENHAIN referred to the allotropic forms of iron known as α , β , and γ iron. It might be that the β form was a case of dynamic allotropy, and there was a possibility of mutual solution of the two forms within certain limits of temperature. The "infectious" nature of "tinpest" was of great interest and importance; analogous phenomena were to be found in the case of severely-strained steel and in other instances. The volume-changes accompanied by disintegration that took place in some of the aluminium alloys were probably to be ascribed to allotropy.

Prof. T. TURNER likewise drew attention to the possibility of allotropic forms existing in other metals, such as lead and zinc.

Mr. J. W. HINCHLEY said it would be of great interest to know whether there were any retarding agents that would prevent the metastable from passing to the stable states. He thought that lead acted in this way towards tin.

Mr. G. T. HOLLOWAY asked whether tin could be prepared so pure that "infection" would not take place in it.

Mr. W. R. BOUSFIELD remarked that spongy platinum deposited from a chloride solution containing only one-fortieth per cent of lead was black and velvety. This might possibly be an allotropic form. He thought that in the case of antimony one did not have allotropy but a solid solution of minute quantities of chloride in the body of the metal.

Dr. H. BORNIS believed that foreign substances had been found in the explosive form of antimony.

Dr. E. FEILMANN referred to the mysterious giving way of lead sheet in acid chambers which might be due to allotropy.

Prof. E. COHEN replied briefly to the discussion. He did not think the re-crystallisation referred to by Professor Ewing had anything to do with allotropy. Replying to Mr. Holloway, he had experimented with tin containing only 1/500 per cent impurities. He could not answer Mr. Bousfield's question. The two forms might merely be different states of division, but he would look into the matter. Replying to Dr. Borns, there were always traces of the acid of the solution from which it was deposited in explosive antimony. It was often overlooked that electro-deposited substances almost always contained traces of the solution mechanically enclosed.

NOTICES OF BOOKS.

Systematic Qualitative Analysis. By R. M. CAVEN, D.Sc. (Lond.), F.I.C. London, Glasgow, Dublin, Bombay: Blackie and Son, Ltd. (3s. 6d. net).

THE first part of this book dealing with the general principles of qualitative analysis is well written, and would be likely to give the student a good grasp of the theoretical basis of analytical chemistry. The second part contains the reactions of the metallic and acidic radicals and separation tables, while Part III. consists of detached analysis tables, which merely summarise the methods which have already been thoroughly studied. The tests described are those which are generally employed, and there appear to be no specially novel features to recommend the book. It is, however, very systematic and thorough, though the too lavish use of footnotes would perhaps give the lazy student a chance of overlooking some important matter.

Elementary Chemical Theory. By J. M. WADMORE, M.A. (Oxon.). London: Methuen and Co., Ltd. 1911. (3s. 6d.).

THIS book is intended for the use of schools, and contains all the chemical theory which can profitably be studied by boys and girls of the school age. The treatment is quite elementary, and the author frequently makes use of very simple similes to explain his subject and give his young readers clear and definite views upon modern theories of molecular and atomic structure. The book is divided into short chapters, each treating of one subject, and, as far as possible, complete in itself. The author realises very vividly the need of emphasising what might appear obvious to older readers, and making his explanations clear even at the expense of brevity. There are undoubted advantages to be gained from putting into the hands of students textbooks dealing only with the theory of chemistry, to supplement those in which descriptive and theoretical chemistry are treated side by side, and this is a very suitable book for the use of beginners.

A Laboratory Manual of Inorganic Chemistry. By EUGENE C. BINGHAM, Ph.D. (Johns Hopkins) and GEORGE F. WHITE, Ph.D. (Johns Hopkins). London: Chapman and Hall, Ltd. New York: John Wiley and Sons. 1911. (1.00 dol. net; 4s. 6d. net).

ALTHOUGH the students of Richmond College, Va., where the authors of this book are Professor and Assistant Professor respectively, may find it convenient for use for their first year's course in inorganic chemistry it is difficult to see why it should be offered for wider circulation. The treatment of the subject is neither particularly novel nor specially suitable for large classes of students, and the instructions are in some cases nothing more than the rules in force at this particular college. The course is divided into three parts. In the first some important inorganic preparations are described, and the second deals with qualitative analysis. The third part gives some quantitative work, which would not appear to be quite suitable for elementary students; it includes atomic weight determinations and the finding of molecular weights. There is occasionally some looseness of expression in the text which is an unsatisfactory feature, as, for example, the classification of substances for analysis into classes which distinctly overlap.

Continental Price Calculator. By W. G. CHAPMAN. London: Effingham Wilson. 1911. (5s. net).

By means of this book English prices can be instantly converted into their foreign equivalents at the current rates of exchange, without any calculation whatever. It allows for the fluctuations of the exchange, and includes both lengths and weights in all Continental measures. The convenience of the tables will at once be apparent, and

practical men will find them most useful when dealing with foreign clients. The tables, while giving the values of all English prices in the foreign denominations, do not give all foreign values in terms of English; thus to find the equivalent of, say, 4 marks in shillings at 20:30 would require a short calculation.

Organic Chemistry for the Laboratory. By W. A. NOYES, Ph.D. Second Edition. Easton, Pa.: The Chemical Publishing Company. London: Williams and Norgate. 1911. (2.00 dols.).

IN the second edition of this book the order of the chapters has been altered so as to agree more closely with that adopted in the author's text-book of Organic Chemistry, and much new matter has been added. This includes the description of a large number of preparations of typical compounds of importance and also new chapters on the hydroxy and ketone acids, the carbohydrates, and the ethers. The book contains detailed descriptions of many preparations, from which a thoroughly satisfactory course of practical organic chemistry could be mapped out, and if before performing the experiments the student were to look up the literature of each preparation as given in the very full lists of references he would lay a good foundation for organic research work. A chapter has been added to the new edition dealing with the qualitative examination of carbon compounds and methods of identification of different classes of derivatives.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 20, May 15, 1911.

Action of Ultra-violet Rays on Lactic Acid.—Marc Landau.—When lactic acid is exposed to the rays from a mercury lamp gases are evolved consisting of about 90 per cent of carbon dioxide and some carbon monoxide. Oxygen is not formed. Besides evolving gases lactic acid undergoes other transformations, various substances being formed, e.g., ethyl alcohol, and traces of pyruvic acid, as well as a substance, not yet identified, which colours a solution of fuchsin reddish violet, the colour being removed by sodium bisulphite and sulphuric acid, and which reduces Tollens' reagent in the cold.

Presence of Zinc Nitrate in Zinc Powder and in Commercial Zinc.—Camille Matignon.—Zinc nitrate appears to exist in all commercial zinc powders, and it is also found in certain zincs, but always in extremely small quantities. Specimens of zinc white do not contain it.

Definite Compounds of Arsenic and Tin.—Pierre Jolibois and Eugène L. Dupuy.—Different authors have stated that the following compounds of arsenic and tin exist:— Sn_6As , Sn_3As_2 , SnAs , Sn_2As_3 , Sn_3As_4 . Metallographical examination indicates the existence of two definite compounds, As_3Sn_4 and AsSn . Crystals of As_3Sn_4 can be obtained by electrolysis, an alloy with 7 per cent of arsenic being the soluble anode with ferrous chloride as the electrolyte. The properties of the two compounds are very similar.

New Method of Etherifying Alcohols by Hydroacids.—G. Darzens.—When an alcohol is treated with thionyl chloride in presence of a tertiary base B the following irreversible reaction occurs—



Thus isoamyl alcohol in presence of diethyl aniline gives a quantitative yield of isoamyl chloride. Similarly the hydrobromic ethers can be obtained with thionyl bromide. The phenol function cannot be etherified thus.

THE CHEMICAL NEWS.

VOL. CIV., No. 2695.

APPLICATIONS OF PHYSICAL CHEMISTRY TO THE DOCTRINE OF IMMUNITY. ANTIGENES AND ANTIBODIES.*

By Prof. SVANTE ARRHENIUS, D.Sc., Hon.F.R.S., Hon.F.C.S.
Director. Nobel Institute of Physical Chemistry.

I. Introduction.

THE doctrine of antigenes and antibodies is of very recent date. The first systematic investigations in this field, which has developed so rapidly and become of enormous importance, are due to Behring and Kitasato (1890). It is quite natural that attempts should be made to systematise and explain the vast material collected, in order that there should be a general survey of the field of work. The most prominent fact is that it is generally possible, by injection of different substances of organic origin into the veins of an animal, to obtain from the blood of that animal a serum which neutralises the action of the injected substance. This is called "antigene"; the active neutralising body in the blood-serum is called "antibody."

It seems rather natural to compare this neutralisation between antigene and antibody with the very familiar neutralisation process occurring on mixing an acid with a base. This idea was at first developed by Ehrlich, who was prevented by the great difficulties he encountered from carrying out his conceptions. These difficulties are largely dependent upon the slowness of the reaction of these substances, with the incompleteness of their reactions, and with the instability of the reagents. A great number of investigations regarding these phenomena have been made by Madsen in Copenhagen, and by myself. I will now try to describe the more general features of the results of these and similar studies.

Many of the antibodies are obtained by the injection of red blood corpuscles into the veins of animals. Some of these antibodies possess the property of causing hemolysis, *i.e.* red blood-corpuscles of the same kind as the injected ones, under the influence of these antibodies, give up their red colouring matter, the hemoglobin, to the surrounding fluid, which is thereby coloured red. This is easily observed if the blood-corpuscles are allowed to subside for a certain time, generally twelve to twenty-four hours, in an ice-safe. The strength of the colour may be measured colorimetrically, so that quantitative results are easily obtained. Such antibodies are called hemolysins, and play an important role.

Other antibodies obtained in this manner are called agglutinins, because they agglutinate the red blood-corpuscles to aggregates which subside or stick to the walls of the vessel containing the emulsion of blood-corpuscles from animals of the same species as the injected corpuscles. In this case, as in experiments on hemolysis, the blood-corpuscles are separated through centrifugation from the blood-serum, and then suspended in a solution having their own osmotic pressure, in general 0.9 per cent solution of sodium chloride; otherwise the blood-corpuscles may be attacked by the surrounding fluid itself. For instance, pure water hemolyses red blood-corpuscles very rapidly.

If bacteria are injected, the blood-serum contains substances which may attack the bacteria, so that they slowly disappear—those antibodies are called bacteriolysins—or the antibodies may agglutinate the bacteria, then they are called bacterio-agglutinins. These antibodies, just as the hemolysins, are very specific, so that they do not react

with other bacteria except those which were injected. They are therefore used to discriminate bacteria from each other, which is of great use in determining the cause of illnesses. The high degree of specificity indicates a chemical action.

If a fluid antigen, as common egg-white or blood-serum, is injected, the serum of the injected animal contains an antibody called precipitine, because on mixing with egg-white or a serum of the same kind (*i.e.* taken from an animal of the same kind) as that injected a precipitate is formed. Even this reaction is in a high degree specific.

II. Spontaneous or Catalytic Destruction of Antigenes or Antibodies.

A great number of these substances are rapidly destroyed at high temperatures (over 50° C.). In order to find the rate of destruction, one determines the relative quantities which are necessary to add to the reacting substance, *e.g.* a given quantity of a standard emulsion of red blood-corpuscles or bacteria, or a given quantity of an albuminous substance, in order that the reaction—hemolysis, agglutination, precipitation—shall be of the same order of magnitude. Madsen and his pupils have performed a great number of such experiments. It was found in all cases that the laws of physical chemistry govern this phenomenon. As an instance, I give the figures for the

Spontaneous Destruction of Dissolved Tetanolyisin at 49.8° C.

<i>t</i> (minutes)	<i>e</i> , observed	<i>c</i> , calculated
0	100.0	100.0
20	80.0	80.6
40	61.1	64.8
60	52.1	52.3
80	46.3	42.1
120	26.8	26.7
180	14.6	14.3

Tetanolyisin is a very strong poison secreted by tetanus-bacilli, whereby they cause lock-jaw (tetanus). The close agreement between the calculated and the observed figures of its strength *c* indicates that the simple law, which says that 50 per cent of the poison is destroyed in about sixty-four minutes, 75 per cent in double the time, 128 minutes, and 87.5 per cent in the threefold time, 192 minutes, is very nearly exact. That is the law of molecular reactions, when every reacting molecule—here every molecule of the poison—is decomposed independently of every other molecule in the solution, except perhaps of the water itself. It is necessary to keep the temperature very accurately constant, because it has an extremely great influence on the rate of decomposition. Thus, for instance, this rate is 16.7 times greater at 53.5° than at 49.8°, *i.e.* the tetanolyisin loses its half strength in a little less than four minutes at 53.5°. An increase of as little as 0.1° C. increases the rate of decomposition by 8 per cent. An increase of 1° accelerates the decomposition 2.14 times.

In general, the stability of these bacterial poisons is largely influenced by temperature.

As Madsen has remarked, this property may be useful for the animal body, which generally reacts against these poisons by an increased temperature, *i.e.* fever.

An addition of alkali or acid mostly accelerates the process in a high degree. Many of these preparations contain a little alkali in their original state. Then an addition of acid increases their stability. In such cases even diluted solutions may be more stable than more concentrated ones.

But, in general, these preparations, and even the antigenes, are most stable in the form of dry powder, and are decomposed the more rapidly the higher the dilution. This is the case, for instance, with rennet, as is seen from the following figures of Madsen and Walbum, valid for 46° C.

* A Discourse delivered at the Royal Institution, June 9, 1911.

Concentration per cent.	Velocity of decomposition.
7	0.0037
5	0.0049
3	0.0154
2	0.0212
1	0.028
0.5	0.032
0.25	0.039
0.125	0.060
0.063	0.073

Dry rennet is very much more stable: it is not decomposed in a sensible degree at temperatures below 100° C.; at 158° C. the velocity of decomposition is only 0.071. The higher stability in higher concentrations probably depends on the formation of compounds with albuminous substances contained in these preparations, which are more stable than the antigen or antibody itself, and which are decomposed at higher dilutions.

Some albuminous substances diminish the stability. Thus Madsen and Walbum found that an addition of Witte's peptone increases the rate of decay of tetanolsin.

As has already been said regarding tetanolsin, the rate of decomposition increases very rapidly with temperature. This increase is subject to the same law as is found for common chemical reactions, namely, that an exponential formula is valid, *i.e.* the velocity of reaction increases in a certain proportion for every degree. Thus Madsen and Famulener found for a hemolysin from goat-serum:—

Temperature (°C.)	Velocity of decomposition.	
	Observed.	Calculated.
51	0.0139	0.0145
51.5	0.025	0.024
52	0.038	0.038
52.5	0.060	0.060
53	0.095	0.095

This law is verified for a great number of substances in their spontaneous decomposition as well as in their decomposition through the presence of foreign substances, such as acids or bases, or in the case of tetanolsin, of Witte's peptone. When foreign substances act catalytically the influence of temperature generally is not so great as in spontaneous decomposition, but nearly of the same order of magnitude as in common catalytic processes—the velocity of reaction increases in the proportion of about 1 : 2 or 1 : 3 if the temperature rises 10° C.

III. Velocity of Reaction of Antigens on other Substances.

Many of these reactions are of such a nature that only a certain phase of the process may be accurately determined. Thus, for instance, during the coagulation of milk by the aid of rennet, the moment when the milk contained in a test-tube does not change its surface at a slight inclination of the tube, may be rather accurately determined. After that the milk gets more and more viscous, but still no suitable method of determining the times corresponding to these higher degrees of viscosity has been found. Something similar is also true regarding the agglutination. A certain degree of agglutination may be determined with comparative accuracy, but not others. In similar cases the time necessary to bring about just that degree of coagulation or agglutination has been studied, when different quantities (*q*) of antigens have been used. It has been invariably found that the greater the quantity (*q*) the less the time (*t*), so that in most cases the product (*q.t*) was constant. Madsen investigated for instance the digestion of gelatin by means of pepsin by adding to a mixture of a solution of 2 cc. of a 7 per cent solution of gelatin and 1 cc. of 0.4 per cent solution of HCl, 1 cc. of a solution containing different quantities (*q*) of pepsin. The mixture was heated for two hours to 36.6° C., and then put in an ice-safe, where it soon solidified, if it was not digested. By trying a great number of mixtures

containing different quantities (*q*) he found the least quantity (*q*₂) necessary to cause just that degree of viscosity, as described above, in two hours. In the same way he determined the quantity (*q*₄) necessary to give the same degree of fluidity in four hours and so forth. He found the following values:—

Time (t).	Quantity of pepsin (q).	Product (q.t).
2	0.47	0.94
4	0.26	1.04
8	0.13	1.04
14	0.07	0.98
20	0.045	0.90
24	0.038	0.91

The product (*q.t*) is not wholly constant, but very nearly so. The law for common monomolecular reactions, where the rate of chemical change is proportional to the quantity of the acting substance, is fulfilled. In a later experiment Madsen maintained the quantity (*q*) constant, and determined the time necessary for the given degree of digestion at a given temperature. This time is evidently inversely proportional to the velocity of reaction. He found the same regularity in this case as for the change of other chemical reactions with temperature (*cf.* above).

Similar regularities were found for the digestion of gelatin by means of trypsin or an antigen, produced by pyocyanus-bacilli, in the coagulation of milk by means of rennet, in the coagulation of blood-plasma, &c. It is sometimes found that the velocity of reaction has a maximum at a certain temperature, which is explained by the fact that the spontaneous decomposition of the antigen increases very rapidly with rising temperature and much more rapidly than the reaction investigated. At high temperatures, therefore, the time during which the antigen, *e.g.* rennet, really has opportunity to react, is practically zero, and the observed reaction extremely small. From this circumstance the occurrence of a maximum is easily understood. In the coagulation of milk by means of rennet, Fuld observed such a maximum at 43° C. In reactions of living cells on other substances such maxima are generally found at about 40° C., at which temperature the cells slowly lose their vital activity by the coagulation of their protoplasmic content. Such maxima are often found in this department of science; they depend on the concurrence of two simultaneous processes which act in opposite directions. In many of these processes, for instance the coagulation of milk or of blood-plasma, the presence of certain salts, in most cases salts of calcium (salts of barium or strontium act in a similar manner), play an important rôle. Reichel and Spiro found for the coagulation of milk that the necessary time is inversely proportional to the concentration of calcium-ions in the solution.

IV. The Peptic Digestion, Schütz's Rule.

The most interesting reaction of this kind is the peptic digestion of albuminous substances. E. Schütz found that the quantity of pepton formed during a given time is proportional to the square root of the adopted quantity of pepsin. Later investigations by Sjöquist, Henri, and Bayliss proved that with a constant quantity of pepsin the digested quantity (*i.e.* the quantity of pepton) is proportional to the square root of the time of digestion; or, generally, that the digested quantity is proportional to the square root of the product of quantity of pepsin used and time of digestion. This rule is called Schütz's rule, after its discoverer.

It was believed for a long time that this rule was peculiar to the action of organic ferments; it is also found in the action of trypsin on albuminous substances, and of lipases from the pancreatic juice, or from castor beans, on fats, as well as for the peptic or tryptic digestion of coagulated albuminous substances, and for the action of proteolytic ferments, *e.g.* from malt. It had not been found for common chemical processes. Then I proved, theo-

retically as well as experimentally, that the same rule holds good for the saponification of esters with great excess of ammonia. The peculiarity depends upon the formation of ammonium salts in the process itself. According to the law of mass-action, the acting number of hydroxyl-ions is lowered in a high degree through the presence of the ammonium-ions of the ammonium-salt formed, so that after a short time the number of acting hydroxyl-ions is very nearly inversely proportional to the quantity of salt present. In this case Schütz's rule holds good as indicated by a mathematical analysis of the process, and experiments verified this conclusion. But the calculation indicates that this rule should not be applicable further than until about 50 per cent of the ammonia is consumed, and it is easy to deduce the general law for the whole process. The same was found to be the case for the action of the examined ferments of organic origin. Thereby it was proved that these phenomena depend upon an interaction between the products of decomposition and one of the reacting substances of such a nature that the really active part of that substance is inversely proportional to the quantity of reaction-products formed. The antigenes or ferments have also in this case their analogies in general chemistry.

The mathematical analysis of these cases shows that the decomposed quantity is only dependent on the magnitude of the product $q \cdot t$, where q is the quantity of ferment used and t is its time of action. These processes are therefore monomolecular.

Cases have been observed in which the reaction-products do not exert this influence upon the reacting substances. The reacting substances were in this case of a relatively low molecular weight, but in their properties were similar to albuminous substances or to fats, namely, glyceryl-glycin and triacetin. In the digestion of glyceryl-glycin with erepsin, an extract from the stomach, Euler found that the general law for undisturbed monomolecular reactions is valid. The same was found by A. E. Taylor for the saponification of triacetin by means of extract from castor beans. This corresponds to the saponification of an ester by means of sodium hydrate in great excess. This circumstance seems to indicate that the reaction-products, in the cases for which Schütz's rule is valid, act on the albuminous substances or fats and not on the ferments.

V. Processes in Heterogeneous Systems.

In processes in heterogeneous systems the same laws are found to be applicable. But a certain part of the acting substance, for instance, a hemolysin or a bacterio-agglutinin, is necessary to induce any action at all, still more if a certain easily measurable action—in these cases a hemolysis of e.g. 30 per cent of the blood-corpuscles, or the very accurately observable degree of agglutination—would be obtained in say one hour at 37°C . In such cases the reaction does not, generally, proceed very much further with time. Therefore the rule, that the product qt of reacting substance and time of reaction regulates the phenomenon, does not hold good for such low concentrations as those just spoken of, but only when the reacting substance (i.e. the hemolysin or bacterio-agglutinin) is present in a considerably greater quantity. In such cases a correction is made for the quantity just necessary to produce a sensible effect. This rule has been verified by Madsen and myself for the hemolytic action of ammonia; by Madsen and Henderson Smith for the hemolytic action of tetanolysin; and by Madsen for the agglutinating effect of Coli-agglutinin, which agglutinates *Bacillus Coli*. The following figures for hemolysis by means of ammonia may serve as an instance. The figures give the time in minutes necessary for obtaining a certain degree of hemolysis, i.e. percentage of the emulsinated blood-corpuscles hemolysed at 37°C . The process was carried to an end by rapidly cooling the test-tubes to 0° and centrifuging the red blood-corpuscles at this low temperature.

Degree of hemolysis in per cent.	Attenuation of the ammonia.			
	$1/q : 1$	$1/q : 0.44$	$1/q : 0.23$	$1/q : 0.133$
3	13 (13)	6 (5.7)	—	—
10	26 (26)	10 (11.5)	5.5 (6.0)	—
20	35 (35)	15 (15.4)	9 (8.0)	4 (4.7)
30	44 (44)	18 (19.4)	12 (10.1)	6.2 (5.9)
40	53 (53)	23 (23.3)	14 (12.2)	8 (7.1)

The figures calculated according to the $q \cdot t$ rule are written in brackets at the side of the observed ones. The agreement is quite satisfactory having regard to the magnitude of the errors of observation. Even acids act as of hemolysins.

As is well known, water itself acts as a weak base and acid, and therefore acts as a hemolysin. Gros observed that red blood-corpuscles, emulsinated in an isotonic cane-sugar solution, are completely hemolysed in 18.8 minutes at 50°C , in 45.5 minutes at 56°C . This corresponds to an increase in the velocity of reaction in the proportion of 1 to 19 in an interval of 10°C . Madsen determined the increase of the velocity of reaction in the hemolysis by means of acids, bases, and hemolysins of bacterial origin, such as streptolysin and vibriolysin. He observed an increase in the proportion of about 1 to 4 in an interval of 10°C . For some snake-poisons, e.g. those from *Naja tripudians* or *Ancistrodon* (water-moccasin) he observed maxima of action at a certain temperature. The cause of these maxima is still unexplained.

Strong acids react much more rapidly than weak acids; but if small doses are used, so that a considerable time (e.g. twelve hours) was necessary for the reaction, the strong acids (e.g. HCl) acted only about 1.25 times stronger than very weak ones (e.g. acetic acid) used in equivalent quantities. This indicates that a real chemical union takes place, which causes the hemolysis. A similar remark may be made regarding the bases. The action of acids is very much increased if the blood-corpuscles have been treated for some time (twenty minutes) with a weak emulsion of lecithin. Oleic acid, and other fatty acids of high molecular weight, act more strongly than other acids.

In these reactions the hemolytic or agglutinating substance is rather rapidly taken up by the red blood-corpuscles or bacteria; but it takes some considerable time—the so-called time of incubation—till hemolysis begins. This indicates that it is a rather slow chemical process which causes the hemolysis or agglutination, after the hemolysing or agglutinating substances are united to substances in the interior of the treated cells.

VI. Partition of Hemolysing or Agglutinating Substances between Cells and the Surrounding Medium.

If we allow an emulsion of red blood-corpuscles or bacteria to stand for some time with a hemolytic or agglutinating substance dissolved in an isotonic solution of e.g. sodium chloride, the substance is absorbed rather rapidly by the emulsinated cells. We may therefore centrifuge away the cells and examine the remaining fluid as to its contents of acting substance. By these means it is possible to determine the rate of partition of the said substance between the cells and the surrounding solution. If we wish to avoid hemolysis, it is necessary to work at a low temperature (near 0°). A shaking up of the cells now and then is also desirable.

In this manner, Madsen and Teruchi found that vibriolysin is divided between red blood-corpuscles and the fluid, so that the concentration of vibriolysin in the cells is about 230 times greater than in the fluid. This was proved by treating different quantities of cells from 0.05 up to 0.6 cc. with 9.95 resp. 9.4 cc. of salt-solution, charged with a certain quantity of the poison. In the first case (0.05 cc.), the cells took away 56 per cent of the poison; when the cells were eight times as many, 90 per cent. The two determinations give ratios of partition of 254 : 1 and 227 : 1, which may be regarded as equal, if we consider the great errors of observation.

I observed the same property in a more indirect way, namely, by means of the observed degree of hemolysis. If this is constant, the red blood corpuscles are in the same state, independently of their number, and the surrounding solution has the same concentration of the poison. If, then, I investigate different quantities of red blood-corpuscles in the same quantity of isotonic salt-solution, and add just so much poison that a certain fraction—say 40 per cent—of the blood-corpuscles is hemolyzed, then the same quantity of poison is in the fluid, and the blood-corpuscles have taken up a quantity of poison proportional to their number. By changing this number, it is possible to determine how great a part of the poison remains in the fluid, and how much is taken up by each cc. of the suspended blood-corpuscles. Of course, it is necessary always to use the same temperature—I had a bath of 37° C.—and time of reaction—I used two hours—in the same series of experiments. In this manner I found that for saponin the concentration in the blood-corpuscles was 120 times greater than in the solution. For ammonia, caustic soda, and acetic acid, I found values varying between about 600 and 900 times. I have found similar high values for silver salts and mercuric chloride, which are also hemolysing substances.

This strong absorption of the blood-poisons in blood-corpuscles indicates that they are probably chemically bound to some substances in the cells. The absorption proceeds, according to Madsen's and Teruchi's experiments, in agreement with common physico-chemical laws, *i.e.* in proportion to the excess of the concentration in the fluid over that concentration which would be in equilibrium with the poison absorbed in the cell at the time observed.

Those antibodies which have been examined hitherto behave in a somewhat different manner. Eisenberg and Volk allowed certain kinds of bacilli, *viz.* typhoid-bacilli or cholera vibrios, to be emulsified for a certain time with solutions of different quantities of the corresponding agglutinins, dissolved in a given quantity of 0.9 per cent solution of sodium chloride. The bacillus slowly subsided, and the supernatant fluid was decanted and its content of agglutinin determined. It was then found that the concentration in the bacilli increased more slowly than the concentration in the fluid, and proportional to the power two-thirds of this concentration. This circumstance indicates that the molecular weight of the agglutinin in the bacilli is only two-thirds of its molecular weight in the surrounding fluid. If the agglutinin has entered as a chemical compound in the bacilli, then the quantity of agglutinin in each molecule of this compound is only two-thirds of the quantity of agglutinin in each agglutinin-holding molecule in the fluid.

As is said above, after injection of red blood-corpuscles of one animal into the veins of another animal, we find in the blood-serum of the second animal a substance which hemolyzes the red blood-corpuscles of the first animal. This hemolysin loses its hemolytic properties if it is heated for some time to 56° C. But it still contains a substance, called immune-body, characterised by the fact that it gives a hemolysin specific to red blood-corpuscles of the first animal if it is mixed with some innocuous serum, *e.g.* serum from guinea-pigs. By means of this property it is possible to determine the quantity of immune-body contained in a certain volume of a fluid. The absorption of immune-body in the red blood-corpuscles of the first animal has been investigated by Morgenroth and myself. In this respect it behaves exactly as the agglutinins.

As instances the following measurements of Eisenberg and Volk regarding cholera-vibrios, and of Morgenroth and myself regarding red blood-corpuscles from an ox may serve. The absorbed substances were in the first case agglutinin against cholera vibrios, in the second immune-body contained in serum of a rabbit, treated with red blood-corpuscles from an ox. T is the total quantity of one of these substances in an arbitrary unit, B that part of

it which remained in the fluid, C the absorbed quantity. The following equations are used for the calculations:—

$$B + L = T; \quad L = K B^{2/3}.$$

Absorption of Cholera-agglutinin.

T	C	B. obs.	B. calc.	K
2	2	0	0.03	—
20	20	0	1.0	—
40	38	2	2.8	24
67	60	7	6	16.4
200	120	80?	27	—
2,000	1,300	700	620	16.5
11,000	6,500	4,500	5,200	23.9
20,000	10,000	10,000	10,750	21.5

Mean 19

Absorption of Immune Body from Rabbit-serum.

T	C	B obs.	B calc.	K = 18.3
250	226	27	39	
330	275	55	57	
670	500	170	151	
1,330	850	480	376	
2,700	1,710	990	942	
5,000	3,070	1,930	2,050	
10,000	5,800	4,200	4,800	
16,700	7,800	8,800	8,870	
33,000	13,900	19,100	19,700	

The agreement between the observed and the calculated figures may be regarded as quite satisfactory. The change of the values of B, the observed quantity, are extremely great (in the proportion of 1 to 5000 in the one case and 1 to 800 in the other), and the errors of observation are relatively important. Under such circumstances it may be regarded as proved that the equation given above represents the phenomenon with a high degree of accuracy.

(To be continued).

EIGHTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1910.*

By F. W. CLARKE.

(Concluded from p. 16).

Scandium.

PRELIMINARY determinations of the atomic weight of scandium, by the sulphate method, are given by Meyer and Winter, but without the detailed weighings (*Zeit. Anorg. Chem.*, lxxvii., 398). The values found for Sc range between 44.86 and 45.37; in mean, 45.12. This is much higher than the accepted value.

Neodymium.

By very careful analyses of neodymium chloride, Baxter and Chapin have determined the atomic weight of the metal (*Proc. Am. Acad.*, 1910, xlvii., 215; reproduced in

Ratio NdCl₃ : 3Ag.

Weight NdCl ₃ .	Weight 3Ag.	At. wt. Nd.
4.27402	5.51855	144.283
2.79574	3.61030	144.249
2.77391	3.58196	144.259
3.42064	4.41695	144.267
4.11855	5.31786	144.280
3.95958	5.11289	144.266
4.64435	5.99699	144.271
Mean		144.268

Journ. Am. Chem. Soc., January, 1911). Two ratios were measured, with vacuum weights, and reduced with $\text{Ag} = 107.880$ and $\text{Cl} = 35.457$.

Ratio $\text{NdCl}_3 : 3\text{AgCl}$.		
Weight NdCl_3 .	Weight 3AgCl .	At. wt. Nd.
3.16218	5.42546	144.257
2.93305	5.03226	144.262
2.99149	5.13195	144.289
2.62468	4.50338	144.250
2.38439	4.09064	144.278
2.55827	4.38891	144.280
3.59114	6.16095	144.277
4.27402	7.33203	144.293
4.69459	8.05144	144.264
2.79574	4.79030	144.280
2.59810	4.45741	144.270
3.42064	5.86872	144.265
4.11855	7.06518	144.298
3.95958	6.79345	144.262
2.71834	4.66395	144.257
Mean		144.272

A slight correction for a little unseparated praseodymium raises the value to 144.275. This is doubtless the best determination of the constant yet made.

Erbium.

Hofmann, by analyses and syntheses of the sulphate has made three new determinations of the atomic weight of "neoberbium" (*Ber.*, xliii., 2635).

Weight Er_2O_3 .	Weight sulphate.	Weight Er_2O_3 .	At. wt. Er.
0.3117	0.5070	0.3117	167.67
0.4486	0.7296	0.44863	167.73
0.3718	0.6048	0.3718	167.64
Mean			167.68

The oxide in the first column was converted into sulphate, which, on calcination, gave the oxide of the third column. Calculated with $\text{S} = 32.07$.

The Helium-Argon Group.

Watson has determined the weight of a normal litre of helium as 0.17814 and 0.17830 gm. (*Journ. Chem. Soc.*, xcvi., 810). Hence $\text{He} = 3.994$. For neon, eleven determinations of the normal litre ranged from 0.8997 to 0.9006 gm.; in mean, 0.9002. This, by the method of limiting densities, gives $\text{Ne} = 20.200$. By the same method Watson (*Journ. Chem. Soc.*, xcvi., 833) has reduced the densities of krypton and xenon, as measured in 1908 by Moore (*Proc. Chem. Soc.*, xxiv., 273). The final values are $\text{Kr} = 82.92$ and $\text{Xe} = 130.22$.

The density of argon has been re-determined by Fischer and Hähnel (*Ber.*, xliii., 1435). The mean of seven determinations is 19.945, referred to $\text{O} = 16$. Hence $\text{A} = 39.89$.

Ramsay and Gray, by means of the microbalance, have been able to weigh the gaseous emanation of radium, for which they propose the name *niton* (*Comptes Rendus*, cli., 126). The values thus found for its molecular weight are 222, 216, 227, 218, 217, in mean 220. The same value was also found by Debiere by a different method (*Comptes Rendus*, cli., 1740).

Miscellaneous Notes.

Richards and Baxter have investigated the subject of density corrections, or, in other words, the reduction of weights to a vacuum (*Journ. Am. Chem. Soc.*, xxxii., 507). They regard the validity of the corrections, as applied at Harvard, as well established. Relations between the atomic weights have been studied by Howard (*CHEMICAL NEWS*, ci., 181, 265). Dubreuil has continued his recalculation of the determinations of Stas (*Bull. Soc. Chim.*, [4], vii., 119).

ON THE CONNECTION BETWEEN THE VOLATILITY, FUSIBILITY, AND DENSITY OF COMPOUNDS, AND THE CHEMICAL FORCES AT PLAY WITHIN THEIR MOLECULES.

By GEOFFREY MARTIN, B.Sc., M.Sc., Ph.D.

PROF. RICHARDS points out in his suggestive Faraday Lecture to the Chemical Society (published in abstract in *CHEMICAL NEWS*, July 7) that the more strongly the atoms are chemically united or attracted together in the molecule (as judged by the heat of formation), the denser (*i.e.*, more contracted) is the resulting compound, and he goes on to suggest that the forces of chemical attraction actually compress the atom themselves.

May I be allowed to point out that this is but a particular case of a wider generalisation published by me some years ago in my book "Researches on the Affinities of the Elements" (J. and A. Churchill, 1905). For example, I showed in that work that there exists a similar relationship between the chemical forces uniting the atoms in the molecules of a compound and the volatility, fusibility, and hardness of the compound. It is this: the more strongly attracted together are the atoms in the molecule (and therefore the more stable the molecule) the more strongly attracted together are the molecules themselves, and consequently the greater is their cohesive force, involatility, and infusibility. By taking practically all the known data I showed that as a class *chemically unstable bodies* (*i.e.*, bodies in which the atoms in the molecules are but feebly attracted together) are characterised by their *volatility, fusibility, and lack of hardness*—properties depending upon molecular attraction (cohesive force)—whereas *chemically stable compounds* (*i.e.*, compounds in which the chemical forces uniting the atoms in the molecule is great) are characterised by their *involatility, infusibility, and hardness*. In other words, it is the *internal chemical forces which the atoms exert on each other in the molecule which decides the external attractions with which the molecules themselves are attracted together and consequently properties arising out of this molecular attraction, such as volatility, fusibility, hardness, and density of the compound* (see "Researches on the Affinities of the Elements," pp. 68 et seq., 111, 120, 123; also *CHEMICAL NEWS*, 1904, lxxxix., 241, "The Connection between the Volatility of Compounds and the Chemical Forces at Play within the Molecule"). It is therefore very doubtful whether the fact quoted by Prof. Richards is a good reason for assuming that the atoms themselves are really compressible. The fact of the matter is that the chemical forces exerted by the atoms so enormously transcend any other forces that they exert, that they almost completely decide all the properties, both chemical and physical, exhibited by any molecular aggregation of matter—a conclusion also arrived at in my essay, and there examined in detail.

Ureins of *p*-Oxyphenylaminoacetic and *p* Methoxyphenylaminoacetic Acids.—J. Aloy and Ch. Rabaut.—By applying the method of Hugouenq and Morel to *p*-oxyphenylaminoacetic acid and the corresponding *p*-methoxy acid the authors have prepared the mixed ureas and the symmetrical ureins of both acids. The mixed urea of the former exists in the form of white crystals, fusing at 198° , very slightly soluble in water and soluble in alcohol. The properties of the other mixed urea are very similar; its melting-point is 193° . When heated the mixed ureas decompose, setting free aniline. The symmetrical ureins are prepared by the action of COCl_2 on the sodic solutions of the corresponding acids. They are both yellow substances; that derived from *p*-oxyphenylaminoacetic acid decomposes when heated, but the other compound is more stable.—*Bull. Soc. Chim. France*, ix., No. 6,

AN IMPROVED FUNNEL.

By PHILIP BLACKMAN.

THE funnel is made of glass of various sizes, and its shape is that shown in section in the figures. There are two special dimensions, viz.:—

1. From A to B (diametrically) is at least 1 inch (and greater in larger sized funnels).
2. The height B to C is not less (preferably somewhat more) than the distance A to B.

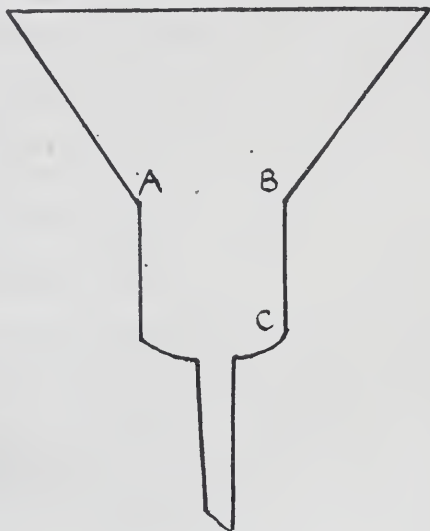


FIG. 1.

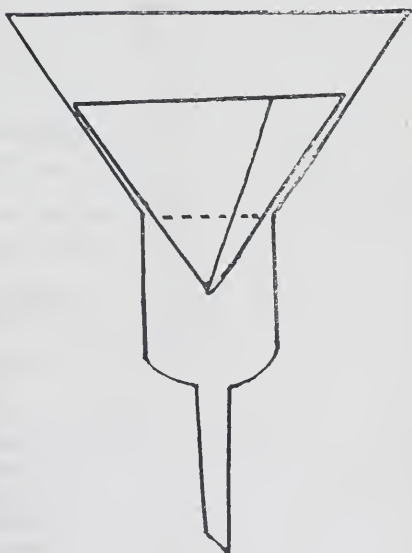


FIG. 2.

Advantages.

1. In an ordinary funnel the filter-paper fits very closely the funnel sides, and thus the passage of liquid through the filter is greatly retarded. In the funnel here described a great part of the filter cone, all or nearly all that part containing liquid or precipitate, is suspended, and has no

contact with the funnel (see Fig. 2), thus affording more perfect and greatly accelerated filtration.

2. A fluted or ribbed funnel is difficult to clean; this funnel needs no flutes or ribs.

3. A fluted filter-paper, on account of the creases meeting at the centre, is liable to tear or give way at the apex of the cone. With this funnel the necessity for fluted filters disappears.

A FUNNEL-SUPPORT.

By PHILIP BLACKMAN.

THE support here described is made of glass. It consists of a circular disc, in various sizes (from 4 to 12 inches in diameter), with a number of concentric circular flutes or

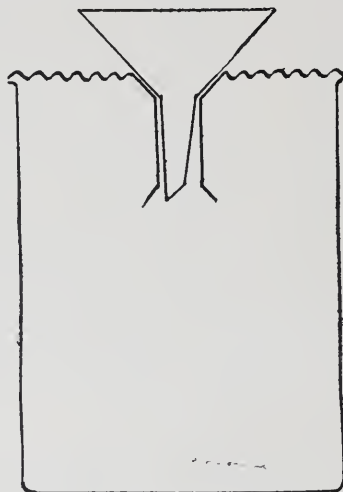


FIG. 1.

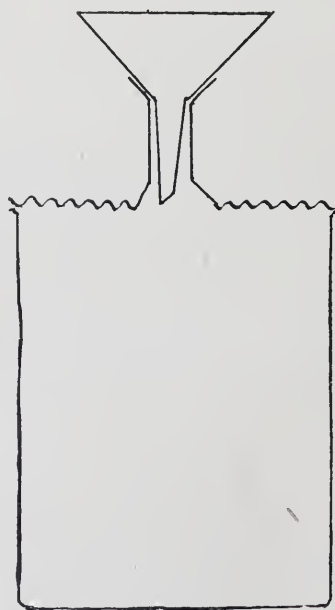


FIG. 2.

ribs (both the width and depth of each flute or rib being approximately one-third of an inch), and having at the centre an upright tube ($1\frac{1}{2}$ inches in length and of uniform internal diameter of half-an-inch), each end being funnel-shaped so that a funnel may fit in and rest without shaking.

Advantages.

1. It will fit any beaker of smaller diameter than its own, and will hold any sized funnel.
 2. The flutes or ribs prevent slipping from the rim of the beaker.
 3. There are no adjustments requisite.
 4. It may be used in an inverted position to suit depth of beaker or length of funnel-stem.
 5. It prevents dust from falling upon a filtrate.
 6. It prevents evaporation of a filtrate.
 7. It is less clumsy in use than the ordinary funnel-stand, it takes up no lateral space, there are no screws to manipulate or heights to adjust, and it is very easily capable of being maintained clean.
 8. It may be used with any other wide-mouthed vessel.
- The figures represent sections through funnel, support, and beaker, in one the support being used in a normal position, in the other in the inverted position.

THE BOILING-POINTS OF METALS.*

By H. C. GREENWOOD, M.Sc.

THE experiments which form the subject of the present communication have been already briefly described in *Proceedings of the Royal Society*, 1909, A, lxxxii., 396; and 1910, A, lxxxiii., 483. It was thought, however, that as the subject possesses not only scientific interest, but has also important bearings on metallurgy and its allied industries, a description of the investigation giving more experimental details might be of interest.

The primary object of the experiments was to fix approximate values for the boiling-points of a number of metals, and thus clear away the very considerable uncertainty which existed in most cases. They were afterwards extended to a consideration of the dependency of the boiling-points on the pressure. The existence of such a dependency is in itself an important criterion of any method for fixing the boiling-points, particularly when dealing with the high temperatures necessary to effect the ebullition of most metals.

The problem first received attention in 1879 from Carnelley and Williams (*Trans. Chem. Soc.*, 1879, p. 563), who attempted to determine the temperature of the vapours of a few metals by suspending tubes containing metals of known melting-point above the surface. To take an example of their results, there is little doubt that the value for tin is at least 700°C . too low. Since these experiments, very little has been done in the way of a systematic determination of metallic boiling-points. Féry (*Annales de Chimie et de Physique*, Sér. F, xxviii., 428), however, determined the boiling-point of copper in 1903 by optical measurements in an arc furnace and also effected the fractional distillation of brass. The arc furnace is unsuitable for such measurements on account of the difficulties of power regulation and of temperature estimation. Moissan (*Comptes Rendus*, 1906, cxlii., 425), in the course of an extensive investigation on the vaporisation of metals in his arc furnace, obtained values giving the weight volatilised in a certain time under given conditions. From these experimental results Watts has attempted to deduce approximate values for the boiling-points of the metals (*Trans. Am. Electrochem. Soc.*, 1907, xii., 141). Great uncertainty is due to the considerable vapour tension possessed by many metals at temperatures well below their boiling-points, to the total lack of data giving the latent heat of

TABLE I.

I.			
Time from commencement.	Temperature.	Current.	
Minutes.	Degrees.	Ampères.	
12	1800	320	Clear and still.
13	1820	320	Do.
14	1860	320	Clear, gentle agitation at edges, centre still.
15	1905	330	All surface in gentle agitation, no drops thrown up.
16	1915	330	Do.
17	1935	330	Drops thrown up very gently.
18	1935	330	Do.
19	1955	330	Drops quite decided.
20	1955	330	Drops thrown half-way up crucible.
21	1965	330	Drops sent out of crucible.
22	1975	330	Do.
II.			
16	1770	260	Perfectly clear and still.
18	1815	260	Do.
20	1860	260	Do.
21	1875	290	Slight traces of movement at edges.
22	1880	290	Surface quiet.
23	1915	290	Gentle agitation, no drops thrown up.
24	1925	290	Do.
25	1955	290	Decided agitation, drops thrown up gently.
26	1955	300	Do.
27	1975	300	Drops half-way up crucible.
28	1975	300	Vigorous, drops projected out of crucible.
29	1980	300	Do.
III.			
6	1440	330	Clear and still.
9	1560	330	Do.
12	1670	360	Do.
13	1730	360	Do.
16	1790	360	Do.
18	1840	370	Do.
20	1860	370	Slight agitation at edges.
21	1880	380	Do.
22	1900	380	Clear, gentle agitation all over surface.
24	1920	380	Agitation decided, no drops thrown up.
25	1935	390	Agitation decided, occasional drops.
27	1955	390	Drops sent up decidedly.
29	1980	390	Drops vigorous, half-way up crucible.
30	2000	390	Drops projected out of crucible.

vaporisation, and further to the fact that the actual energy expenditure in the furnace was apparently not measured by Moissan. Moreover, this is greatly influenced by the conductivity of the vapours surrounding the arc, and many of the results are of little value by reason of the carburisation which took place. No other data were available with the exception of some values arrived at in vapour density determinations (*cf.*, Mensching and Meyer, *Annalen*, 1887, ccxi., 317; and Wartenberg, *Zeit. Anorg. Chem.*, 1908, lvi., 320), and the general position was so unsatisfactory and the data actually available so discordant that further investigation was urgently needed. With regard to the effect of pressure, only ebullition under very low pressures (Kraft, *Ber.*, 1903, xxxvi., 1690) had been studied, except for metals like zinc of comparatively low boiling-point (Barus, *Bull. U.S. Geolog. Survey*, No. 103; *Phil. Mag.*, 1890, [5], xxix., 141). The main reason for this was the

* A Paper read before the Faraday Society, May 23, 1911.

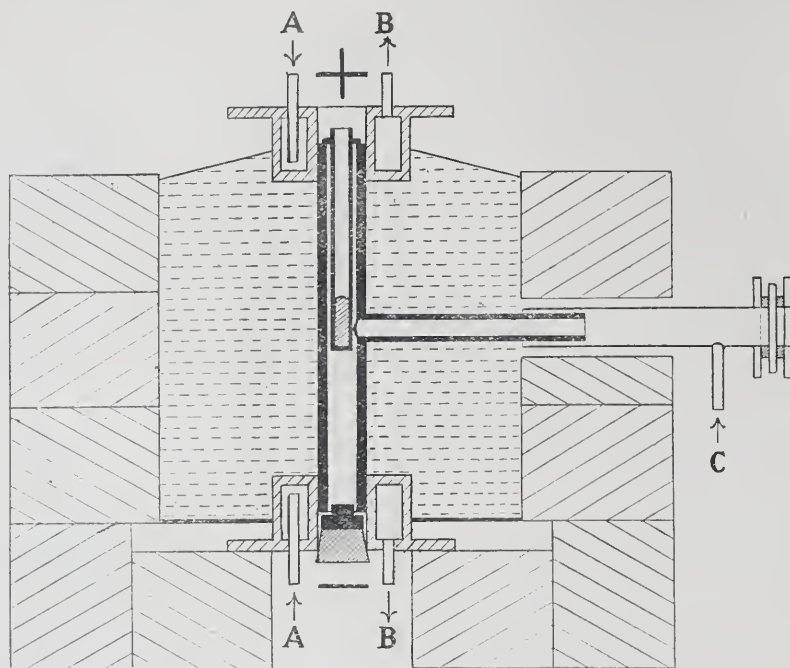


FIG. 1.

difficulty of finding any material capable of withstanding reduced pressures at temperatures above 1400°C. , and the consequent necessity for limiting the temperature by the use of very high vacua. This difficulty was avoided in the present experiments by arranging the whole furnace inside a vacuum enclosure.

The investigations may be divided into three main sections:—

1. A study at atmospheric pressure of the boiling-points of a number of metals which do not combine appreciably with carbon (antimony, bismuth, copper, lead, magnesium, silver, tin).
2. A study at atmospheric pressure of the boiling-points of some metals which are readily attacked by carbon with the formation of carbides (aluminium, chromium, iron, manganese).
3. The influence of diminished and increased pressures on the boiling-points of certain of the metals under 1 (bismuth, copper, lead, silver, tin, zinc).

PART I.—Non-carburisable Metals.

In some earlier experiments carried out by Dr. L. Bradshaw the loss in weight of the metal maintained at fixed points over a wide range of temperature was determined. The loss by volatilisation, however, was found to take place over such a large temperature interval that in the present investigation other methods were adopted. Experiments were carried out in which a considerable quantity of metal, contained in a thin-walled graphite crucible, was heated in a carbon tube resistance furnace so chosen that the temperature could be quite rapidly raised, it being hoped that when the metal entered into ebullition a discontinuity in the rise of temperature would be observed, as shown by optical temperature readings on the outside of the crucible. Such, however, was not the case, the temperature of the walls rising considerably above the boiling-point of the metal. It was eventually found that the best results were to be obtained by gradually raising the temperature of the metal and taking observations of the surface from above through an absorbing glass. The surface at first remains perfectly still, but on approaching

the boiling-point a slight agitation is observed to set in, which rapidly becomes vigorous. In most cases the difference between the temperatures indicated, when a gentle agitation is first apparent and when the ebullition is so vigorous that globules of metal are projected to a height of over 10 cm., does not exceed 100° . By taking the boiling-point as that temperature at which ebullition first becomes decided, quite concordant results were obtained in different experiments (*cf.*, records of experiments given in Table I.).

From observations of a number of metals in this manner it seems probable that the boiling-point may with fair approximation be taken as the temperature at which the vaporisation becomes sufficiently vigorous to cause a decided projection of drops from the surface (*e.g.*, 1955° in the above cited three experiments with silver).

In most of the experiments the furnace employed was of the vertical carbon tube resistance type (see Fig. 1), tubes 25 cm. long and of 20 and 30 mm. internal diameter respectively being used. The ends were electro-coppered and soldered into brass castings provided with water circulation at A and B, and a side tube of carbon was fitted to the centre of the resistor, and continued at the other end by a brass fitting furnished with a window. The whole was packed in crushed wood charcoal, this being a good heat insulator, and also desirable as regards absence of vapours at high temperatures. Suspended and fitting fairly closely inside the resistance tube was a long graphite crucible, made as thin as possible (about 1 mm.) in the walls, and containing the charge of metal. This form of crucible acts as a reflux condenser, and the amount of metal does not rapidly decrease. Graphite being an excellent conductor of heat, the error due to temperature difference between the outer and inner surfaces of the crucible walls was thus rendered negligible. A depth of about 30 mm. of metal was ordinarily used, and temperature readings were taken on the walls of the portion thus occupied (this being arranged immediately opposite the side tube) by means of a Wanner optical pyrometer. Freedom from fumes in the side tube was secured by the passage of a current of hydrogen admitted at C. With

This arrangement only the radiation from the crucible walls could fall upon the pyrometer, and a close approximation to black body conditions was obtained.

Using the two sizes of carbon tube mentioned, currents of about 500 and 900 ampères at 8 and 10 volts respectively were required to raise the temperature to 2500° C. moderately quickly. The temperature was under delicate control by manipulation of a rheostat in the field circuit of the separately excited dynamo supplying the current. Although experiments made up to 1500° in comparing the optical temperature readings with those of a thermo-couple immersed in the metal indicated that the difference between the temperature of the metal and that of the outer walls was negligible, it was thought desirable to obtain further proof of this. With this object in view and to make use of a somewhat different method of measurement, the apparatus shown in Fig. 2 was devised, the metal being con-

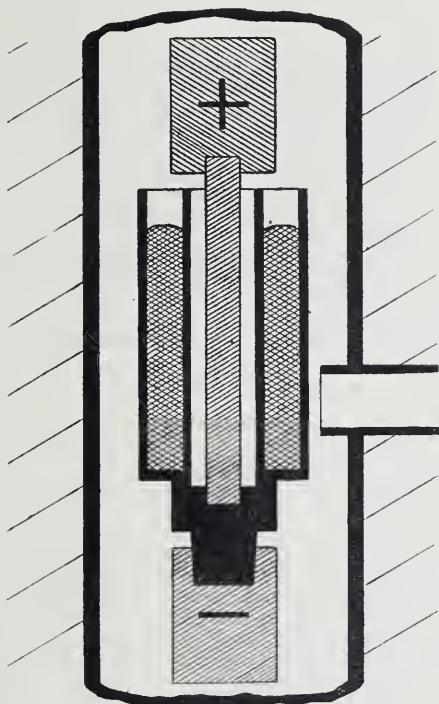


FIG. 2.

tained in the annular portion of a graphite crucible of the form shown, heating being effected internally by radiation from the intensely heated central carbon rod supplied with current from the two thick graphite rods. To attain the boiling-point of lead, *i.e.*, about 1500° C., a current of about 200 ampères at 20 volts was necessary, using a central carbon rod of 9 mm. diameter. The arrangement was fixed inside a wide carbon tube lagged with Kieselguhr, and temperature readings taken on the outside of the crucible down a side tube exactly similar to that used in the apparatus shown in Fig. 1. Here the effect of temperature errors due to imperfect thermal conductivity of the crucible walls is reversed, and the possibility of reflexion from the resistor altogether removed. Experiments with lead gave results in agreement with those obtained by the other method, but it was equally impossible to obtain limitation of the temperature of the outer surface of the crucible when the contents were caused to vigorously boil. It was therefore concluded that the apparatus shown in Fig. 1 was introducing no error due to this source. A curious effect was, however, traced to the current of

hydrogen employed in the side tube of the furnace. If this current were stopped when the metal was gently boiling ebullition ceased. On substitution of nitrogen for hydrogen the temperature readings agreed among themselves in similar experiments, but were always considerably higher (50° to 100°) than those obtained in a hydrogen atmosphere. This curious effect is probably to be explained by the ease with which hydrogen diffuses through the crucible walls, dislodging the heavy vapours above the surface of the metal.

That this action actually occurred could be distinctly seen by interrupting and then suddenly restarting the current of hydrogen whilst looking down the crucible. Measurements were in most cases made with both nitrogen and hydrogen, but it seems probable that the results obtained with the use of the latter approximate more closely to the true boiling-points at atmospheric pressure.

Accuracy of the temperature measurements was ensured by the insertion of an ammeter and rheostat in the standard lamp circuit of the optical pyrometer. Comparison with a thermoelement up to 1500° showed that the readings closely agreed with the thermoelectric temperatures (due allowance being made for the difference between the two scales). A further check was secured by determining the "black body" melting-points of strips of platinum, rhodium, and iridium specially prepared in a high state of purity by Messrs. Johnson, Matthey, and Co. These strips, which were 4 mm. wide and 8 cm. long, were mounted horizontally and heated electrically. A series of results obtained for the melting-points of these metals is given below.

TABLE II.

Platinum (deg.).	Rhodium (deg.).	Iridium (deg.).
1545	1670	1995
1560	1655	1985
1555	1680	2025
1545	1680	1990
—	1680	2035
Mean 1551	1673	2006

The values given by Holborn and Henning (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, xii., 311) for the "black body" melting-points are as follows:—Platinum 1545°, rhodium 1650°, iridium 2000°. Seeing that the readings obtained with this optical pyrometer are now capable of reference to some definite standard, it was thought best to publish the results without further correction, all temperatures being given on the optical scale.

In the following table will be found a list of the boiling-points experimentally determined, and also of the data previously available.

In the case of magnesium the boiling-point was determined by the use of a protected thermocouple immersed in the metal, the temperature remaining steady while the metal distilled into the upper portion of the crucible.

TABLE III.

Metal.	Previous data.		Author's values.
	Authority.	Values.	
Copper ..	Féry	2100°	2310°
Tin	Wartenberg	Above 2200°	2275°
	Carnelley and Williams	1435—1505°	
Silver ..	Wartenberg	Above 2200°	1955°
	Carnelley and Williams	2070°	
Lead ..	Wartenberg	1435—1505°	1525°
	Carnelley and Williams	1580°	
Bismuth ..	Wartenberg	1084—1435°	1440°
	Carnelley and Williams	1550°	
Antimony .	Barus	1084—1435°	1420°
	Carnelley and Williams	Above 1437°	
	Mensing and Meyer	1500—1700°	
Magnesium	Biltz and Meyer	1100°	1120°
	Ditte	Above 2200°	

(To be continued).

DUCTILE TUNGSTEN AND MOLYBDENUM.*

By COLIN G. FINK, Ph.D.

TUNGSTEN has heretofore been known chiefly as a steel-hardening metal. In recent years, however, it has become an important material for filaments of incandescent lamps, and is to-day the most efficient metal for the purpose, owing to its high melting point (3000° C.), which is higher than that of any other metal, and its low vapour tension.

It is well known that tungsten is described in all of the text-books as a brittle grey metal, and that numerous attempts have been made to reduce it to ductile form, as is evidenced by publications emanating from various research laboratories. Roscoe and Schorlemmer, in the latest edition of their "Treatise on Chemistry," state that "the purest forms of tungsten at present obtainable are hard and brittle and are not ductile, either at ordinary temperatures or when heated."

The metal has ordinarily been obtainable in commerce form of a dark gray powder, usually made by the reduction of yellow oxide by hydrogen or by carbon. This powder, when bought on the open market, is generally impure, and is purified by various well-known methods, particularly if the method is to be used for filaments of incandescent lamps. These filaments have been made on a large scale and are in common use in this country and abroad. Even in ordinary commercial lamps, the filaments are of a degree of purity so high that no impurities can be discovered by the most searching methods of chemical analysis known. Not only is this true, but these filaments, during the course of chemical production, are exposed to temperatures high enough to drive out by mere vaporisation almost any impurity.

Nevertheless, these filaments show no traces whatever of ductility, or even pliability, but on the contrary, though strong enough for mounting in commercial lamps, they are exceedingly brittle and incapable of taking a permanent set. Attempts have hitherto been made—but always without success—to produce ductile tungsten by various purification processes, varying the ore from which the tungsten is obtained by trying first wolframite (an iron-manganese tungstate) and then scheelite (the calcium tungstate). Whichever ore is used, it is customary to produce from it the yellow oxide, and a high degree of purity has been sought by repeated precipitations. Various methods of reduction have been tried; among other reducing agents, hydrogen, carbon, aluminium, zinc, and magnesium have been used. Reduction has also been effected by electrolytic methods. Since tungsten metal produced in this way has been so pure that no impurities could be detected by ordinary chemical or physical means, and has yet retained its characteristic hardness and brittleness, it has generally been concluded that the metal is entirely lacking in that physical property which is ordinarily termed ductility.

Announcement has recently been made, however, of the production of tungsten in a form in which it is ductile. This ductile tungsten would seem to be a new substance from the point of view of the physical chemist, and it has seemed to me that this society would be interested in learning something of the properties of this product, since only those of us who have been connected with the Research Laboratory of the General Electric Co. have as yet had an opportunity to study it.

Ductile tungsten is a bright, tough, steel-coloured metal, which can be drawn into the finest wire, much below one-thousandth of an inch. The tensile strength of the wire increases as the drawing proceeds; or, in other words, the more the metal is mechanically worked, the tougher and stronger it gets. In the following table a few figures on the strength of tungsten wires are given. They are the average obtained from a large number of measurements:

TABLE I.—Tensile Strength.

Tungsten Wire.				
Diam. in mm.	5.0	2.8	1.5	1.2
	0.125	0.070	0.038	0.030
Lbs. per sq. in.	460,000	480,000	550,000	580,000
	to	to	to	to
	490,000	530,000	600,000	610,000
Kg. per sq. mm.	322	336	385	406
	to	to	to	to
	343	371	420	427
Molybdenum Wire.				
Lbs. per sq. in.	200,000	230,000	270,000	
	to	to	to	
	260,000	270,000	310,000	
Kg. per sq. mm.	140	161	189	
	to	to	to	
	182	189	217	

A piece of hard drawn piano wire, tested with the same apparatus, registered, on the average, 507,000 lbs. (35 kg. per sq. mm.), the diameter of the wire being 3-thousandths of an inch (0.075 mm.). According to Schnabel, aluminium shows a similar behaviour as regards the effect of drawing: cast aluminium gives but 17,000 lbs. per square inch (11.9 kg. per sq. mm.), whereas the drawn metal has a tensile strength of 36,000 to 39,000 lbs. (25.2 to 27.3 kg. per sq. mm.).

The density or specific gravity values of ductile tungsten likewise increase with the amount of working. The values of ductile molybdenum were also determined at our laboratory.

TABLE II.—Specific Gravity.

Tungsten.		Molybdenum.	
Before Drawing.		After Drawing.	
18.81		10.02	
Diameter.			
Inches.	mm.		
0.150	3.75	19.30 to 19.30	10.04
0.010	0.25	19.58 to 19.64	10.29
0.0015	0.038	19.86 to 20.19	10.32

Martin (1907) found the density of melted tungsten, analysing 98.96 per cent pure, to be 16.28; Moissan (1896) and Weiss (1910) give the values of 18.70 and 18.72 for the brittle metal. As is seen from the table, the density increases very appreciably with the amount of mechanical working applied. This same phenomenon is well known in the case of copper, zinc, and other metals. The density of cast copper according to Marchand and Scheerer is 8.92, and that of rolled and hammered copper 9.95. Distilled zinc gives 6.92 and wrought zinc 7.25.

The electrical resistance and the temperature coefficient of the two metals are given in Table III. We used the Wheatstone bridge method. The resistance was measured at room temperature and at 170°, employing two oil thermostats.

TABLE III.

	Resistivity (25°) in microhms per cub. cm.	Temp. coeff., per degree between 0° and 170° C.
Tungsten	d. 6.2	0.0051
	a. 5.0	
Molybdenum	d. 5.6	0.0050
	a. 4.8	

The values marked *d* are for hard drawn wire; those marked *a* were obtained after annealing. This resistivity value for tungsten is a good deal lower than that given by Gin (*Trans. Am. Electrochem. Soc.*, xiii., 483). The coefficient for copper (0° to 160°) is 0.00445 (Reichardt); the registry values for copper are 1.62 for the hard drawn and 1.58 for the annealed wire.

The hardness of both tungsten and molybdenum depends very much upon the amount of mechanical working

* A paper presented before American Electro-Chemical Society from the *Chemical Engineer* (Chicago), xii., No. 2.

to which the metals have been subjected, and also upon the presence of impurities. Whereas the hard varieties scratch glass, the soft varieties are easily cut with a file.

The thermal coefficients of the two metals were determined on wire 5-thousandths of an inch in diameter. A reading of one degree on the scale was equivalent to an elongation of the wire of 0.000545 inch. The values obtained are 336×10^{-8} for tungsten and 360×10^{-8} for molybdenum, the temperature range being 20° – 100° . The platinum value for the same range is 884×10^{-8} (Dulong and Petit).

Chemically, the two ductile metals behave similarly in many respects. The drawn wire retains its lustre almost indefinitely. Both metals are readily attacked by fused oxidising salts, such as NaNO_3 , KHSO_4 , and Na_2O_2 . Acids (HCl , HNO_3 , H_2SO_4) attack tungsten very slowly, but molybdenum rather readily. I have heated fine drawn tungsten wire in a mixture of chromic and sulphuric acids for sixteen hours, but could detect only a very small loss in weight.

Original weight: 16.7330 grms.; after sixteen hours, 16.7329 grms.

Original weight: 1.3638 grms.; after fourteen hours, 1.3635 grms.

Apparently the metal becomes passive just like iron.

NOTICES OF BOOKS.

Introduction to Chemistry. By WILHELM OSTWALD. Authorised Translation by WILLIAM T. HALL and ROBERT S. WILLIAMS. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1911.

THIS book is based upon the same principles as those which contributed so largely to the success of the author's "Schule der Chemie." The latter, however, was written in the conversational form in which the always intelligent and interested pupil asked apposite leading questions and never non-plussed his teacher by unanswerable queries. This style made the book lively and amusing to read, but was hardly suitable for the use of the beginner, for whom this adaptation of it is intended. It is unnecessary to say that it will make him use his reasoning power and think about his work. The general principles of chemistry are specially emphasised, and instructions for illustrative experiments which can readily be performed by the student are given. In the descriptive portion of the book the commonest elements, including some metals, are treated.

Notes on the Fertilisers, Farm Foods, Seeds, and Pest Remedies Act (Cape Province). By Dr. C. F. JURITZ, M.A., F.I.C. Reprinted from the *Agricultural Journal* of the Union of South Africa. 1911.

THESE notes give fuller explanations of some points in connection with the Fertilisers, &c., Act, passed by the Cape Legislature in 1907, which might present a difficulty to merchants or farmers. They are written more especially to assist farmers to understand scientific terms, and the time, nature, and value of a merchant's warranty. Some discussion of various types of fertilisers is added, and the principles of commercial valuation are explained.

Lehrbuch der Mathematik. ("Text-book of Mathematics"). By Dr. GEORG SCHEFFERS. Second Edition. Leipzig: von Veit and Co. 1911.

THIS text-book of mathematics has been written more particularly for students of science and technics, and is specially suitable for the use of those who are working alone. It provides a good introduction to analytical geometry and the differential and integral calculus, and assumes only the minimum of previous mathematical knowledge, including algebra up to the solution of simple equations and the elements of plane geometry. Many

examples are worked out in full, all being chosen so as to have some direct bearing upon the scientific work of the student. The author has revised the second edition in accordance with some of the criticisms passed on the first edition; for instance, the chapter on Fourier's series has been re-written, and many new examples have been added.

CORRESPONDENCE.

PRECIPITATION OF ALUMINIUM HYDROXIDE IN THE GRANULAR FORM.

To the Editor of the Chemical News.

SIR,—A note by W. E. Taylor appeared in the *CHEMICAL NEWS* of April 13th (vol. ciii., p. 169), describing the precipitation of alumina in a granular form, easily filtered and washed. According to the author, this is achieved by carrying out the precipitation at a temperature of 66°C .

I have tried the method, using alum solutions containing from 0.26 gm. to 0.07 gm. of alumina per 100 cc. These were mixed with ammonium chloride, raised to 66°C ., and precipitated by adding ammonia solution, also at 66°C ., and the mixture was then boiled as directed. In every case the precipitate obtained was gelatinous. On filtering, the precipitate caked in the usual way, and there did not seem to be any increase in the rate of filtration or washing. Other experiments were done, in which no ammonium chloride was added, and again gelatinous precipitates resulted.

It would seem from these results, that temperature is not the only conditioning factor, and that some unstated condition may be the cause of the granular precipitate. A more detailed account of Mr. Taylor's experiments would therefore be welcome—I am, &c.,

RUTH SUGDEN.

Chemical Laboratory,
University of Melbourne,
June 13th, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Anorganische Chemie.
Vol. lxx., No. 3, 1911.

New Quantitative Determination of Fluorine.—Gunnar Starck.—The solution of the fluoride is neutralised with dilute hydrochloric acid, and then a large excess of saturated lead chloride solution is added. The precipitate is allowed to stand over night, and is then filtered off and dried for two hours at 140 – 150° . The precipitate is very heavy, and filtration is easily effected; moreover, the results obtained by the method are very satisfactory.

Binary and Tertiary Alloys of Cadmium, Bismuth, and Lead.—William Edward Barlow.—The author gives the solidification curves of alloys of lead and cadmium, lead and bismuth, bismuth and cadmium, and of the ternary system lead-bismuth-cadmium. In the sixteen alloys investigated there is a transition point at a definite temperature in the neighbourhood of 124° .

Quantitative Determination of Gold by means of Ether.—F. Mylius.—Gold chloride, unlike other metallic chlorides, is soluble in ether, and the amount of gold in a coin can be estimated by shaking the hydrochloric acid solution with ether and distilling off the ether. The maximum error does not exceed 0.01 per cent. The author describes a double salt of gold chloride and copper chloride, $\text{CuAu}_2\text{Cl}_3 \cdot 6\text{H}_2\text{O}$, and gives details of methods of

determining small amounts of silver, lead, iron, &c., with the results of the analysis of many specimens of German and foreign coins.

Action of Hydrogen Peroxide and Sodium Peroxide on Bismuth Salts.—Jos. Hanus and O. Kallauner.—When bismuth nitrate solution is oxidised with ammoniacal hydrogen peroxide solution, yellow preparations are obtained in the cold. They become brown when heated, if sodium peroxide is used. Active oxygen is present in them. They are decomposed by sulphuric acid with liberation of oxygen. Concentrated nitric acid dissolves them slowly in the cold, the colour changing to red brown. The brown products obtained by oxidation with sodium peroxide do not lose their colour when they are boiled for five minutes with water.

Electrical and Mechanical Properties of Alloys of Noble Metals.—Wilhelm Geibel.—The author has determined the tensile strength, electrical conductivity, thermoelectric force, and temperature coefficient of alloys of palladium and silver, palladium and platinum, platinum and iridium, platinum and gold, and gives the results of his investigations in the graphic form.

Determination of Solid Hydrogen Arsenide.—Hans Reckleben and Johannes Scheiber.—Like other arsenic compounds arsenic hydride can be oxidised quantitatively to arsenic acid by ammoniacal silver nitrate solution. It exists in one form only, and has the composition represented by the formula H_2As_2 or HAs . The solid hydride is formed when a dark discharge passes through arseniuretted hydrogen, when the arsenides of the alkali metals are decomposed by water, and when arseniuretted hydrogen is incompletely oxidised by oxygen or air in the cold. The solid hydride is not formed when arsenic is sublimed in a current of hydrogen, nor when arsenic is sublimed by cooling a flame of arseniuretted hydrogen.

Determination of Solid Antimony Hydride.—Hans Reckleben and Johannes Scheiber.—Oxidation by means of iodine solution can be used for the quantitative analysis of antimony precipitates. Under the influence of the dark discharge antimoniuiretted hydrogen gives pure antimony, and it is also obtained when the compounds of antimony and the alkali metals are decomposed by water vapour at the ordinary temperature. Explosive antimony contains no solid antimony hydride, but traces of hydrochloric acid are present in it.

Quantitative Determination of Copper by means of Hypophosphorous Acid.—Jos. Hanus and Arn. Soukup.—The precipitation of copper by means of hypophosphorous acid is not quantitative, the amount of copper remaining in the filtrate depending upon the concentration of the H-ions in the precipitating reagent, upon the length of time the copper remains in contact with the air, and the length of time the oxidised copper is in contact with the acid solution. Only by repeated careful neutralisation can satisfactory results be obtained, and the heating must not be continued too long.

Determination of Silver by Electrolytic Separation from Ammoniacal Oxalate Solution.—F. A. Gooch and I. P. Feiser.—In presence of ammonium nitrate or chloride silver can be separated electrolytically from an ammoniacal solution of the oxalate in the pure state and in a form suitable for quantitative determination. It is best to use a low current, and the electrolysis is completed in twenty-five to thirty minutes.

Constitution of Metatungstates.—Hippolyte Copaux.—On the ground of dehydration experiments the author considers that his formula for metatungstates, $6M_2O \cdot 3H_2O \cdot 24WO_3 + Aq$, is more probably correct than that suggested by Rosenheim, viz., $M_2WO(WO_3)_3(H_2O)_3 + Aq$, and the same formula is confirmed by the crystallographic comparison of potassium metatungstate with potassium silicotungstate and potassium borotungstate.

Bulletin de la Société Chimique de France.

Vol. ix., No. 6, 1911.

Heat of Fusion of Substances Melting in the Neighbourhood of the Ordinary Temperature.—W. Louguinine and G. Dupont.—Van't Hoff's Law states that if T is the absolute temperature of fusion, F is the heat of fusion and K the cryoscopic constant, $F = 0.02 T^2 \frac{K}{K}$.

The authors have determined the conditions in which the constant K can be accurately determined, and have found that with substances melting at the ordinary temperature the law of van't Hoff holds good if they are not viscous in the liquid state and crystallise quickly. If, however, they crystallise slowly and are viscous (e.g., monohydrated sulphuric acid and acetophenone) the value of the cryoscopic constant generally comes out too high. This may be ascribed to the difficulty of determining K correctly in the case of viscous substances.

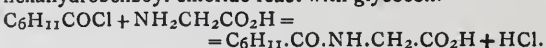
Rôle of Affinity in Dyeing.—A. Rosenstiehl.—In dyeing textiles both cohesion and affinity are called into play, and both forces are necessary to produce the desired effect. If affinity intervenes to produce a coloured layer on the fibre cohesion ensures the adherence of this layer to the fibre.

Determination of Nitrates and Nitric Ethers.—M. Marquoyrol and D. Florentin.—If the values obtained in determining nitrates by means of a nitrometer (taking into account the solubility of NO in sulphuric acid) are compared with those obtained by Schloesing's method, it is found that they agree very well if 94–94.5 per cent sulphuric acid is used. The nitrometer method in certain conditions is accurate, and its rapidity and convenience make it preferable to Schloesing's method.

Quantitative Dehydration of Pure Pinacone.—M. Delacre.—By direct dehydration pure pinacone cannot be made to give a higher percentage of pinacoline than 70 per cent of the theory. Various products are found in the pinacoline which cannot be ascribed to impurities in the pinacone.

Hydrogenation of Essence of Terebenthene.—G. Vavon.—To determine whether an essence of terebenthene is pure it may be subjected to fractional distillation, when at least four-fifths should pass over below 164° . If the product which has passed over between 155° and 158° is subjected to hydrogenation a substance boiling at 166° is obtained if the essence is pure. The volume of hydrogen absorbed ought to be constant for all specimens.

Hexahydrohippuric Acid.—Marcel Godchot.—Hexahydrohippuric acid can be made synthetically by making hexahydrobenzoyl chloride react with glycolol.



The acid chloride required for this synthesis can be prepared by chlorinating hexahydrobenzoic acid with phosphorus pentachloride, while the acid is obtained by treating the bromide of cyclohexylmagnesium with CO_2 —



Preparation of Pseudomorphine by Mineral Catalysis.—Georges Denigès.—The double cyanide of copper and potassium (prepared by adding potassium cyanide to a solution of copper sulphate) can be used as a catalyser to prepare pseudomorphine from morphine chlorhydrate and hydrogen peroxide. The reaction takes place very quickly, and about 20 to 25 per cent of morphine is thus converted into pseudomorphine.

Peroxydiastase of Cow's Milk and the Psrphenylene-diamine Reaction.—E. Nicolas.—Boiled milk gives an indigo-blue coloration with parapsrphenylene diamine and hydrogen peroxide. This coloration is due to the presence of casein, which combines with the product of the oxidation of parapsrphenylene diamine with hydrogen peroxide.

THE CHEMICAL NEWS.

VOL. CIV., No. 2696.

THE DEVELOPMENT OF THE ATOMIC THEORY.*

VI. THE RECEPTION ACCORDED TO THE THEORY
ADVOCATED BY DALTON.

By ANDREW NORMAN MELDRUM, D.Sc.

"FROM the nature of the human mind, time is necessary for the full comprehension and perfection of great ideas." Thus the history of an idea necessarily includes the reception accorded to it on publication, and the steps by which it came to be of influence in the world.

Science, considered as an impersonal thing, advances by assimilating new and sound ideas. Yet this process of advancement, as the following paper shows, depends on the temperaments of individual men. The consideration of paramount importance in this respect is the fact that these men, according to their outlook on matters of theory, can be divided into two classes. There are (1) the men who are alive to the immense value of theory in science, and (2) the men who would confine science to a collection of facts and laws, as if it were "based entirely upon experiment or mathematical deductions from experiment" (P. G. Tait, "Recent Advances in Physical Science," p. 10).

At any given time, the direction in which a particular branch of science advances is determined by a few persons only. Consequently, the men who are inimical to theory may exert a harmful effect on science, by despising and rejecting a theory of the utmost importance.

The usefulness to science of the atomic theory is so completely established now, that it must seem strange to us to observe the efforts Dalton had to make, in order to arouse attention to the importance of his ideas regarding atoms. For some nine years (1801—1810), if not longer, he endeavoured to spread abroad his ideas, both by private communications and publicly, by his writings and by lectures in various parts of the country.

As will be seen, Dalton's speculations had to encounter dangers of two kinds. In the first place, not many people gave themselves much concern about the question of the continuity or discontinuity of matter. They were quite content to go on speaking of "atoms" and "molecules" in a vague, colloquial sense, and Dalton had to induce them, if possible, to use the words as terms of precision. This done, there was always the possibility that they would reject Dalton's idea of an atom as too hypothetical.

His physical atomic theory (described in the fourth paper of this series) was devised in the year 1801, from which time onwards he made many attempts to recommend it to the scientific world. But for years the only avowed adherent which it obtained was William Henry. The question at issue was a fundamental one, and Dalton's finding on it was ultimately triumphant. The theory expressed his conviction that the diffusion of gases is due to physical forces and not to chemical. But the prevailing tendency of the time was to regard diffusion as due to chemical affinity between the gases concerned, and the strength of that tendency was exhibited by the amount of opposition to Dalton's theory. Its opponents included Thomas Thomson, John Murray, T. C. Hope, John Gough, Humphry Davy, and Claude Louis Berthollet.

Dalton's chemical theory was formed by September 6th,

1803,* and he proceeded forthwith to extend and apply it, and make it known in every direction. His first efforts, naturally, were made at this Society, where, on October 7th, he read a paper in which the theory was employed in order to explain the absorption of a gas by water. What he endeavoured to do was to establish a connection between the solubility of a gas and its atomic weight. This paper, as published in 1805, comes to an end with a table of atomic weights, of various simple and compound substances, remarkable as the earliest of the kind ever printed. There is no reason to doubt that the paper contained a table of atomic weights when it was read, but Dalton certainly extended the table before going to press.

Dalton was eager both to have his ideas put into circulation and to have a *résumé* of them put on record. In London, in the winter of 1803-1804, he gave a course of lectures at the Royal Institution, in which he included a brief outline of the theory. He left this for publication in the *Journals of the Institution*, but, as he ironically remarked afterwards, "he was not informed whether that was done" ("New System of Chemical Philosophy," 1808, Preface). Humphry Davy was at the Institution at the time, but Dalton did not succeed in arousing in him any interest in the theory, much less any enthusiasm for it. In a course of lectures which he gave in Manchester in 1805, he included an account of the theory.† But it was not taken up there for years, not even by William Henry. There is not the slightest sign that Dalton would not have welcomed workers on the subject. But the atoms were counted an airy or recondite speculation. Dalton's atomic weight data caused no thrill of excitement, aroused no eager curiosity, no consuming wish to join in his work.

In North Britain Dalton had a different reception. Early in the year 1807 he gave a course of lectures, twice in Edinburgh and once in Glasgow. In Edinburgh he says "a class of eighty appeared for me in a few days." At the conclusion "several of the gentlemen who had attended the course represented to me that many had been disappointed in not having been informed in time of my intention to deliver a course, and that a number of those who had attended a first course would be disposed to attend a second" (Angus Smith, "Memoir of Dalton," p. 58). This reception afforded Dalton precisely the encouragement of which he stood in need. "On these occasions," he said, "he was honoured with the attention of gentlemen, universally acknowledged to be of the first respectability for their scientific attainments; most of them were pleased to express their desire to see the publication of the doctrine in its present form, as soon as convenient. Upon the author's return to Manchester he began to prepare for the press" ("New System of Chemical Philosophy," 1808, Preface).

In the "New System of Chemical Philosophy" both the Preface and the Dedication show that Dalton was immensely grateful for the attention his speculations received in Glasgow and Edinburgh. The dedication runs:—"To the Professors of the Universities and other residents of Edinburgh and Glasgow who gave their attention and encouragement to the Lectures on Heat and Chemical Elements, delivered in those cities in 1807: and to the members of the Literary and Philosophical Society of Manchester, who have uniformly promoted his researches."

An account of the theory, often referred to in this series of papers, had already appeared. Thomas Thomson had

* A paper of his, read before this Society on November 12th, 1802, contains a reference to the chemical theory. This is the paper "On the Proportion of the several Gases, or Elastic Fluids, constituting the Atmosphere." But it was not published till 1805, and Roscoe and Harden think it was re-written in the meantime, for it includes results on the combination of nitric oxide and oxygen, which Dalton did not obtain till August 4th, 1803 (Roscoe and Harden, "New View of the Origin of Dalton's Atomic Theory," p. 35). I cannot myself doubt that this conclusion is the correct one.

† Two unpublished papers, read before the Manchester Society in 1804, probably included accounts of the theory. The titles are respectively "A Review and Illustration of some Principles in Mr. Dalton's Course of Lectures on Natural Philosophy at the Royal Institution in January, 1804," and "On the Elements of Chemical Philosophy."

* *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, IV., Part II.

been so much interested and impressed by the doctrine as Dalton explained it to him in 1804, that he became the first convert to it. He showed as much zeal in the cause as its author. With permission he gave a short sketch of it in the next edition of his "System of Chemistry." This was the third edition, published in 1807, of the most successful treatise of the day on chemistry, and it had more influence, directly, in spreading a knowledge of the doctrine than Dalton's own efforts. It made Dalton's theory known to William Hyde Wollaston in London, to Claude Louis Berthollet in France, and to Amadeo Avogadro in Italy.

Thomson found another opportunity of expounding the theory in his memoir "On oxalic acid," which appeared in the *Philosophical Transactions* of the Royal Society of London in 1808. The very next paper in the *Transactions* is one by Wollaston—on the carbonates and oxalates of potassium—and he, as well as Thomson, advanced his work as exemplifying and justifying Dalton's theory. By these various means, Dalton's and Thomson's books, and Thomson's and Wollaston's memoirs, it became known in Britain and France, in Italy and Sweden.

Not only in these ways, but by personal exertions, Thomson and Wollaston sought to advance the theory. In his "History of Chemistry," Thomson gives a narrative of the efforts that had to be made to induce Humphry Davy to take it seriously. Long as the narrative is, it is quoted here almost in full, for it illustrates the fact that in science the spread of new ideas depends as much on personal efforts, springing from genuine conviction, as on printed papers. It would seem that Thomson and Wollaston failed themselves to persuade Davy. Wollaston, however, converted Davies Gilbert, and he, in his turn, succeeded in converting Davy.

"Some of our most eminent chemists," says Thomson, "were very hostile to the atomic theory. The most conspicuous of these was Sir Humphry Davy. In the autumn of 1807 I had a long conversation with him at the Royal Institution, but could not convince him that there was any truth in the hypothesis. A few days after I dined with him at the Royal Society Club, at the Crown and Anchor in the Strand. Dr. Wollaston was present at the dinner. After dinner every member of the club left the tavern, except Dr. Wollaston, Mr. Davy, and myself, who staid behind and had tea. We sat about an hour and a-half together, and our whole conversation was about the atomic theory. Dr. Wollaston was a convert as well as myself; and we tried to convince Davy of the inaccuracy of his opinions, but, so far from being convinced, he went away, if possible, more prejudiced against it than ever. Soon after, Davy met Mr. Davis (*sic*) Gilbert, the late distinguished president of the Royal Society, and he amused himself with a caricature description of the atomic theory, which he exhibited in so ridiculous a light, that Mr. Gilbert was astonished how any man of sense could be taken in with such a tissue of absurdities. Mr. Gilbert called on Dr. Wollaston (probably to discover what could have induced a man of Dr. Wollaston's sagacity and caution to adopt such opinions), and was not sparing in laying the absurdities of the theory, such as they had been represented to him by Davy, in the broadest point of view.

"Dr. Wollaston begged Mr. Gilbert to sit down, and listen to a few facts which he would state to him. He then went over all the principal facts at that time known respecting the salts; mentioned the alkaline carbonates and bicarbonates, the oxalate, binoxalate, and quadroxalate of potash, carbonic oxide and carbonic acid, olefiant gas and carburetted hydrogen; and doubtless many other similar compounds, in which the proportion of one of the constituents increases in a regular ratio. Mr. Gilbert went away a convert to the truth of the atomic theory; and he had the merit of convincing Davy that his former opinions on the subject were wrong" (Thomson, "History of Chemistry," ii., 293).

Thomson goes on to say that Davy "ever after was a strenuous supporter" of the atomic theory. This puts his support of the theory far beyond its true value. Davy

was never enthusiastic about the doctrine of atoms as such, and he much preferred the term "proportion" to "atom." The following passage, published in 1811, probably represents his mature opinion on the subject:—"it is not, I conceive, on any speculations upon the ultimate particles of matter, that the true theory of ultimate proportions must ultimately rest" (*Phil. Trans.*, 1811, Bakerian Lecture, or Davy's Works, v., 326).

Dalton himself was far from satisfied with the reception accorded to his theory. Hope, of Edinburgh, could not bring himself to accept it (Roscoe and Harden, *loc. cit.* 153). It was criticised adversely by Dr. Bostock in *Nicholson's Journal*, and Dalton, in reply, quoted in support of it analyses by Dr. Bostock. He then remarks:—"A number of such analyses as these would compel Dr. Bostock and others of your chemical readers to examine the theory of chemical combinations which I have offered to them with more attention, than I fear they do. The present state of chemical science imperiously demands it" (*Nicholson's Journal*, 1811, xxix., 150).

In France, also, the theory was coldly received. Berthollet naturally opposed it, for in its general tendency it condemned his attempt to obliterate the distinction between physical and chemical forces, and, in particular, it was contradictory of his doctrine of chemical combination in indefinite proportions (see the first paper of this series). He considered Dalton's theory too hypothetical, and his opposition had great influence. Gay-Lussac, who had been his pupil, was unable to "rid himself of preconceptions due to early training." In his famous memoir, on the proportions by volume in which gases combine, he remained an adherent of Berthollet.

Gay-Lussac was always timid in matters of theory. Such was his temperament. On one occasion he laid it down that "in natural science, and, above all, in chemistry, generalisation should come after, and not before, a minute knowledge of each fact" (*Ann. Chim. Phys.*, 1819, ii., 297). Such a man was not very likely to subscribe to a doctrine like Dalton's, which *promised* to transform the whole province of chemistry. Gay-Lussac admitted the facts adduced by Dalton and Thomson and Wollaston, and that was all.

Gay-Lussac conceded to Dalton as much as he must, and nothing more. From his own results it seems obvious now that there must be very simple ratios between the volumes occupied by different atoms in the gaseous state. Many writers (see, for instance, Clerk Maxwell, "Theory of Heat," 10th ed., 326) have assumed that Gay-Lussac, in his memoir, defined the relation between his law and the atomic theory, but, as a matter of fact, he ignored it. He did not recognise the theory, and the subject was neglected and came to nothing in France for years. At length, in 1814, Ampère published a memoir (*Ann. Chim.*, 1814, xc., 43-86), of which the fundamental idea is that the molecules of different gases under the same conditions have the same size, so that equal volumes of different gases contain the same number of molecules. In this memoir, the first outcome of the modern atomic theory in France, Dalton is not mentioned.

In Italy Amadeo Avogadro had forestalled Ampère by three years (*Journ. Phys.*, 1811, lxxiii., 58-76). Under the stimulus of Dalton's speculations, of which he had learnt through Thomson's "System of Chemistry,"* he composed the memoir in which he advanced and maintained his famous hypothesis, that under the same conditions the molecules of different gases occupy the same volume. This hypothesis, involving as it did a distinct departure from Dalton's ideas, became the fundamental dogma of molecular science only after the lapse of fifty years.

In Sweden J. J. Berzelius had been occupied for some time in determining the composition of metallic salts, when Wollaston's memoir reached him (*Phil. Mag.*, 1813, xli.,

* "In what follows, I shall make use of the exposition of Dalton's ideas which Thomson has given us in his 'System of Chemistry,'" *loc. cit.*, p. 62.

3). Forthwith he set himself the task of testing the validity of Dalton's theory on the grand scale. As he said, "this way of regarding chemical compounds at once throws such a clear light on the doctrine of affinity, that if the hypothesis of Dalton could be proved, it should count as the greatest step that chemistry had made towards its perfection as a science" (*loc. cit.*).

As Lord Morley has pointed out, the people who launch great ideas on the world are seldom the people who apply them. Dalton's and Thomson's efforts to make the atomic theory widely known were really far more valuable than the concrete results they obtained by the use of it. Dalton himself was involved by the theory in a "labyrinth of chemical investigation," where he wandered for many years and wasted his energies. It was Berzelius, and no other, who applied it, made it the foundation of accurate chemical analysis, and proved it to be an organon of incomparable power for the advancement of chemistry.

APPLICATIONS OF PHYSICAL CHEMISTRY TO THE DOCTRINE OF IMMUNITY. ANTIGENES AND ANTIBODIES.*

By Prof. SVANTE ARRHENIUS, D.Sc., Hon.F.R.S., Hon.F.C.S.
Director, Nobel Institute of Physical Chemistry.

(Continued from p. 28).

VII. Influence of Foreign Substances. Sensibilisators.

In many cases it has been found that the presence of certain salts is necessary, or in some cases favourable, for the reactions under consideration. The necessity of certain salts (especially salts of Ca, Ba, or Sr) for the precipitation of casein from milk by means of rennet has already been alluded to. In this case probably a chemical reaction takes place. The coagulation of blood-plasma behaves in the same manner, salts of calcium and analogous metals playing the some rôle as in the precipitation of casein from milk.

In other cases, as in the agglutination of bacilli, the salts seem to exert a similar influence as in the sedimentation of particles suspended in a fluid. The trivalent positive ions, such as Al, act more powerfully than divalent ions, such as Zn, Mg, Cd, and these latter greatly exceed the monovalent ions, such as K or Na. The H-ion has a very strong action. The bases seem to hold back the agglutination just as in the sedimentation of suspensions. These regularities are not very well marked in all cases.

Other substances, especially albumenoids, such as serum from blood or gelatin, diminish the agglutination. The agglutinating cells are probably coated with a thin skin of these albumenoids, whereby their properties become changed.

In hemolysis by means of different bases, such as KOH, NaOH, or LiOH, the presence of their neutral salts has a diminishing action. Equivalent quantities seem to exert the same influence. Madsen and Walbum found that about double the quantity of acid or of base is necessary for complete hemolysis if the red blood-corpuscles are suspended in a salt solution, as when they are suspended in an isotonic solution of cane-sugar. Ammonium-salts have a very strong retarding effect on hemolysis by means of ammonia acetates on the hemolytic action of acetic acid. Probably the velocity of reaction here plays a rôle—under such circumstances this action is easily explained.

Immune bodies, alexins, and agglutinins are, according to experiments of Bordet and Gay, absorbed in a higher degree in red blood-corpuscles if these are suspended in a salt-solution than if they are suspended in blood-serum. The anti-poisonous action of different natural sera may probably be ascribed to this peculiarity. Here evidently a

chemical union of the albuminous substances in the serum plays the chief rôle.

In many cases lecithin has a very strong action. If red blood-corpuscles have been in contact for half-an-hour with an isotonic salt-solution containing only about 3 per cent of an emulsion with 0.1 per cent lecithin, they are hemolysed to the same degree by a certain quantity of an acid, as by the threefold quantity of the same acid, if they have not been treated with lecithin. Probably this action of the lecithin is connected with the double action, one coagulating, and one hemolytic, of the acids. When the coagulation has reached a certain stage, it hinders the hemolysis. On the other hand, treatment with lecithin seems to hold back the coagulation. This gives the explanation of its favourable influence on the hemolytic action of acids. The hemolytic action of bases, which do not coagulate the red blood-corpuscles, is not increased by means of lecithin. Mercuric chloride which possesses also a strong coagulating action, acts more strongly hemolytic on blood-corpuscles if they have been treated with lecithin than on common blood-corpuscles. Lecithin has an extremely great influence on the hemolytic action of cobra-poison. It was believed for a long time that this action was due to the formation of a very strongly hemolytic compound of cobra-poison and lecithin, called cobra-lecithid. Through quantitative experiments I show that neither the cobra-poison nor the lecithin is consumed on the formation of the hypothetical compound, whereby its existence was made very doubtful. Later investigations seem also to indicate that this compound does not exist. The action of lecithin is therefore that of a "sensibiliser" in this case, a theory first enunciated by Bordet in 1898.

There is a case in which lecithin exerts an opposite influence, namely, the hemolysis by means of saponin. Substances which dissolve fats, for instance, alcohols and ether, exert also a weak diminishing influence on the hemolytic action of saponin, but a weak increasing influence on the hemolysis of red blood-corpuscles, treated with lecithin, by means of cobra-poison.

VIII. Neutralisation of Toxins by means of Antitoxins.

We now come back to the central problem in immunochemistry, namely, that regarding the action of antitoxins on toxins. It has, as stated above, been found by Ehrlich that if a certain addition of diphtheria antitoxin neutralises 50 per cent of a given diphtheria poison, then the double quantity is not able to completely neutralise the poison, and even an addition of the three- or four-fold quantity does not make the poison innocuous. This behaviour agrees wholly with the phenomena observed on neutralisation of a weak acid, such as boric acid, with a weak base, such as ammonia. This is seen by a comparison of the two following tables, of which the one relates to the neutralisation of tetanospasmin by means of its antilysin, the other gives the quantity of free ammonia in a mixture of this base with boric acid. In this case the quantity of free ammonia was determined by its hemolytic activity; n is the number of equivalents of antitoxin, or boric acid, added to one equivalent of toxin or ammonia. T gives the quantity of free toxin, or ammonia, in per cent. T calc. is the corresponding quantity calculated according to the law of Guldberg and Waage. The temperature was 37° C.

Neutralisation of Tetanospasmin.

n .	T obs.	T calc.
0	100	100
0.36	70	66
0.72	36	38
1.09	22	23
1.45	14.2	13.9
2.54	6.1	6.3
4.35	2.7	2.9
6.52	1.8	1.9

* A Discourse delivered at the Royal Institution, June 9, 1911.

Neutralisation of Ammonia.

n.	T obs.	T calc.
0	100	100
0.167	85	79
0.333	69	64
0.667	43	42
1.00	25	27
1.333	20	18
1.667	13	13
2.00	10	10

The formula of Guldberg and Waage is in this case:—

$$(\text{Conc. of free lysin}) (\text{conc. of free antilysin}) \\ = K (\text{conc. of combined lysin})^2.$$

The constant K of the equation for the tetanolysin is $K = 0.115$, for the ammonia with boric acid it is 1.02. (Subsequent measurements on the conductivity of borate of ammonia, carried out by Lundén at 37°C ., gave $K = 1.04$ in good accordance with the figure deduced from Madsen's and my experiments).

The agreement between the observed and calculated figures is wholly within the errors of observation. The less the constant K , the stronger is the compound. For strong acids with strong bases the constant K is very small, nearly equal to zero. Even by the neutralisation of toxins the constant K , in some cases, has a very small value.

With the diphtheria-toxin the constant is 0.012, *i.e.* about ten times less than with the tetanolysin, but still the partial decomposition of its compound with its antibody is very evident, as the quoted observations of Ehrlich indicate. But for the lysins in snake-poisons the constant K has still lower values, so that the decomposition of its combination with the corresponding antivenin is nearly insensible except in the neighbourhood of the neutralisation point. This is evident from the following values for the toxicity of one equivalent cobralysin mixed with n equivalents of its antivenin, in its action at 37°C . on blood-corpuscles from the horse.

Neutralisation of Cobralysin.

n.	T obs.	T calc.
0	100	100
0.167	84	83
0.25	71	75
0.333	65	66
0.417	56	58
0.5	44	50
0.667	33	33
0.833	16	16
1.00	3.3	0

In these examples the form of Guldberg and Waage's law indicates that one molecule of poison and one molecule of antitoxin give two molecules of the compound toxin-antitoxin. In other cases, especially with the so-called nerve-poisons, *e.g.* the ricin and the nerve-poisons contained in the snake-venoms, the formula of equilibrium indicates that three molecules of poison combine with three molecules of antitoxin to form two molecules of the compound. This has been regarded as indicating that the hemolysin of the snake-venoms is different from the corresponding nerve-poison, but this conclusion is not necessary; it might be that the compound toxin-antitoxin possesses a molecular weight $4/3$ times as high when it enters in, *i.e.* acts upon the nervous system, as when it enters in the red blood-corpuscles. A similar remark may be made regarding the nerve-poison and agglutinating poison in ricin. There is also another possibility, namely, that the poison as well as the antitoxin, when dissolved in the blood-corpuscles, possess a molecular weight which is only two-thirds of that characteristic of their solution in the nervous substance, and that their compound has a double molecular weight when dissolved in the nerves than when dissolved in the red blood-corpuscles. Many experiments have been made to separate the blood-poison from the nerve-poison, and through the admixture of different substances it has been found possible to change the toxicity in regard to blood in a different proportion from that in

regard to nervous substance. It must here be borne in mind that these admixtures may act as sensibilisers in regard to the blood-corpuscles, but not or only in a lesser degree in regard to the nervous substance, which may explain the effect without supposing that the poison is different in the two cases. This case would then be similar to that of mercuric chloride, which acts both as hemolysing and as coagulating red blood-corpuscles, and through the admixture of lecithin to the blood becomes less coagulating, and thereby more strongly hemolysing. Of course, no one would conclude from this fact that mercuric chloride contains two different poisons. The circumstance that in the preparation of antibodies to a certain poison, for instance, ricin, the strength of the antitoxin in regard to blood is generally nearly proportional to its strength in regard to nervous action, and the corresponding property of different preparations of poison tells very much in favour of the opinion that the blood-poison and the nerve-poison are identical as well as their anti-bodies.

This question is very nearly related to another, namely, the weakening of poisons with time. In this case we very often find that the poison retains its effect of neutralising antitoxin undiminished, whereas its toxicity weakens. This question has been investigated very accurately for tetanolysin and diphtheria poison, because this property plays a very great part in practice. Thus, for instance, a diphtheria-toxin prepared in the Danish State Serum Institute in February, 1902, slowly lost its toxicity, so that it was only half as great in September, 1903, as when it was freshly prepared. Still its power of neutralising antitoxin remained wholly intact, and the constant in the equilibrium formula did not change. This peculiar behaviour was explained by Ehrlich in the following manner. The molecule of the toxin is very complicated and contains one "side-chain" (this term is taken from organic chemistry), which has toxic properties—or, as it is said, contains the toxophorous group—whereas another side-chain binds the antitoxin. With time the toxophorous group decomposes, but the other so-called haptophorous (from Greek, haptēin, bind) group, remains unchanged. The product, called syntoxoid, possesses all the properties of the toxin except that it is innocuous. It has, for instance, the very valuable property of provoking the production of antitoxin when injected in the veins of an animal. The toxicity may be weakened artificially without influencing the binding property, and this circumstance has been much used in preparing antitoxins.

A much more simple explanation is to suppose that there is formed some antisensibiliser in the diphtheria-poison; this preparation contains a great many foreign organic substances which may slowly give new compounds. This antisensibiliser diminishes the action of the diphtheria poison on the nerves, but not on the animal organs—it has been supposed the spleen or the bone-marrow—which produce antitoxin. Further, it does not interfere with the chemical reaction of toxin and antitoxin.

In this manner the extremely complicated hypothesis of Ehrlich, who assumed the presence of about ten different toxic and innocuous substances (the latter called toxoids or toxones) in diphtheria-poison (and even in other poisons), is absolutely unnecessary as regards the syntoxoids. Many of these "partial poisons" have been introduced to explain experimental errors, which were, especially at first, unusually great in this field; another set seek to explain the successively diminishing neutralising power of antitoxin, which depends upon the incompleteness of its chemical reaction with toxin. As a matter of fact, the "side-chain theory" of Ehrlich gives no explanation of the observed phenomena, and has only a very moderate scientific value.

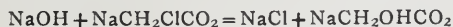
Danysz, a Polish scientist in the Pasteur Institute in Paris, observed a peculiar phenomenon—which has been called, after him, the Danysz-effect—in the neutralisation of ricin or diphtheria poison by their specific antitoxins. He divided the poison into two parts, and in one experiment he mixed a given quantity of antitoxin with both parts simultaneously; in another experiment he added

only the one part of the poison to the same quantity of antitoxin, and after some hours (at 37° C.) he added the second part of the poison. After the poison had had sufficient time to react with the antitoxin, the two mixtures were investigated, and it was found that the second mixture was more poisonous than the first. A similar effect was found later on with tetanolyisin, staphylolyisin, and rennet.

This effect seemed very peculiar; it was, therefore, used by the opponents against the chemical theory of the binding of toxin through antitoxin as an objection against this theory, notwithstanding that they were unable themselves to explain the phenomenon otherwise than by supposing the occurrence in the poisons of some new hypothetical substances, called epitoxonoids. Madsen and Walbum therefore carried out a very great number of experiments regarding the Danysz-effect in regard to tetanolyisin, which I treated theoretically afterwards. I found that the Danysz-effect corresponds to the following well-known chemical process.

Suppose we replace the poison with monochloracetic acid, CH_2ClCOOH , and the antitoxin by an equivalent quantity of caustic soda. If I mix the whole quantity of the acid with the alkali, I get a neutral solution of sodium-monochloracetate, which remains neutral for a long time even at a high temperature (65° C.).

If I in another experiment divide the acid into two equal parts, and mix only the one with the said quantity of caustic soda, at 65° C., then a neutralisation immediately takes place, and there remains a half equivalent of alkali in presence of a half equivalent of sodium monochloracetate. These two substances give rise to a slow reaction, by which sodium chloride and sodium glycolate are formed—



and at the end of this reaction the solution is neutral. If I now add the second half equivalent of the monochloracetic acid, the mixture has a strongly acid reaction, whereas if the two half equivalents of acid had been added to the equivalent of caustic soda, the solution would not have been acid at all.

This phenomenon corresponds wholly to the Danysz-effect. It is evident that no effect would have been found if the quantity of alkali present in the first instance had not exceeded the quantity of acid added—i.e. an excess of alkali is necessary, and the effect is proportional to this excess. Quite the same holds good for the Danysz-effect, as I found by calculation. The experiments had been performed, so that 1 cc. of tetanus poison (a highly diluted preparation) was added to different quantities of antitoxin, and after this mixture had been kept at 37° C., during so long a time that no further sensible chemical change took place, it was mixed with 3 cc. of the tetanus poison. It was found that no effect is observed if the quantity of antitoxin added is less than 0.16 cc. of the solution used. With higher quantities of antitoxin, the effect is proportional to the used quantity diminished by 0.16 cc., just as might be expected. The quantity of antitoxin equivalent to 1 cc. of tetanolyisin was by direct experiments found to be 0.18 cc., which corresponds very well with the 0.16 cc. calculated from the Danysz-effect, especially if we regard the partial decomposition of the compound toxin-antitoxin.

If we had used trichloracetic acid instead of monochloracetic acid, the "Danysz-effect" would have been found to take place in an interval three times as great as the interval of neutralisation, whereas with monochloracetic acid the two intervals are equal. By the action of tetanolyisin on its antitoxin, the interval of the Danysz-effect was found to be more than six times as great as that of neutralisation. This probably depends on the relatively complicated structure of the lysin-molecule.

There are some other peculiar phenomena which are to a certain extent similar to the Danysz-effect. If we take a quantity of a lysin which is just sufficient to cause the total hemolysis of a given quantity of red blood-corpuscles,

and divide this quantity in two equal parts, and add them successively with an interval of some minutes at 37°, to the poison, the hemolysis will not be complete. This depends on the property of the contents of the blood-corpuscles to combine with a quantity of lysin, which exceeds the quantity causing total hemolysis by many, perhaps a hundred, times. The first half of the red blood-corpuscles, therefore, takes away nearly all the poison from the fluid, so that there remains practically no poison at all for the second half of the red blood-corpuscles, which, therefore, remain nearly intact, whereas the first half is totally hemolysed. The result, therefore, is that only a little more than fifty per cent of the total quantity of blood-corpuscles is hemolysed, whereas if all these corpuscles had been mixed with the lysin simultaneously the hemolysis would have been complete.

This observation was made by Bordet; similar effects are found for the agglutination of bacilli by Joos, and they may be explained in the same manner. There is a small secondary effect, as Morgenroth has shown in these cases. The compound of the poison with the content of the cells is partially decomposed, and therefore a small part of the poison diffuses out into the liquid and attacks the cells which were intact before. But this effect is a very slow one, so that it does not disturb the first result very much.

Quite the opposite effect to that observed by Bordet may be stated. Suppose we have so much tetanolyisin that it is just able to give total hemolysis with a certain quantity of red blood-corpuscles. In another vessel we have the same quantity of red blood-corpuscles. Then if we take only the one part of the blood-corpuscles and mix it with the poison, and let it have time to be absorbed, for which a quarter of an hour is sufficient, and then add the second quantity of blood-corpuscles, the hemolysis will be 50 per cent. If, on the other hand, we divide the poison in two equal portions, and add each of them to each part of the blood-corpuscles, then the hemolysis will be much less than 50 per cent, and only about 25 per cent, because the degree of hemolysis of a certain quantity of blood-corpuscles is approximately proportional to the square root of the quantity of poison added. (If this quantity falls below a certain limit, there is no action at all). In this case, evidently, the hemolytic effect is less if we add the whole quantity of red blood-corpuscles at once to the poison, than if we add the two half parts at different times, whereas in the experiment of Bordet the effect was the opposite.

From this effect it is clear that in hemolytic and similar experiments it is necessary to take care that the poison added does not remain for some time in concentrated solutions acting on only a part of the blood-corpuscles, but it is necessary to shake them up immediately after admixture, so that a homogeneous fluid surrounds them. This is most easily done by adding the emulsion of the blood-corpuscles by means of a syringe in a strong current, and shaking the test-tube containing the mixture immediately after the injection of the blood.

Many of the experimental errors in older experiments are due to the circumstance that this precaution has not been followed.

As has been pointed out repeatedly, the poisons are taken up very rapidly by the red blood-corpuscles, or bacilli, into their interior. There they react rather slowly with the albuminous substances, and thus cause the effects of hemolysis, bacteriolysis, or agglutination, which is probably only a special case of coagulation. Therefore, the equilibrium between toxins and antitoxins finds place chiefly in the interior of the cells, and not in the surrounding fluid. The protecting influence of sera and other albuminous substances probably depends on their entering into combinations with the toxins, and thereby hindering them from diffusing into the cells. Many of the difficulties in explaining the effects of toxins and antitoxins were due to the circumstance that it was generally supposed that they react outside of the cells.

(To be continued).

THE BOILING-POINTS OF METALS.*

By H. C. GREENWOOD, M.Sc.

(Concluded from p. 33).

PART II.—Metals which readily Combine with Carbon.

IN dealing with these metals any contact with graphite was of course inadmissible. The difficulty of preventing such contact as these high temperatures proved to be a very serious one, and for long it was found impossible to obtain anything like concordant results. Many attempts were made to utilise the magnesia tubes of the Royal Berlin Porcelain Factory containing vessels. However, even with the most gradual heating, these tubes almost invariably cracked and allowed the contents to flow out. Eventually a method was devised for "brasquing" long carbon crucibles with fused magnesia, though still many of the experiments proved failures owing to the breakdown of the protective lining. Only those experiments in which the lining had remained entire were taken into consideration. Pure magnesia was electrically shrunk by packing round a carbon rod intensely heated by an electric current and subsequently crushed and sieved. The fine powder was kneaded with a saturated solution of magnesium chloride, and by the use of a wooden former a uniform lining 2 mm. thick was obtained. After slowly drying at 200° the crucible was gradually heated up in the furnace (of the type shown in Fig. 1), hydrogen chloride being copiously evolved during the process. The temperature was then allowed to fall somewhat and the charge of metal introduced. Using this method the linings remained perfectly intact and coherent after heating to 1800°, and could be used up to 2500°. At temperatures above 1700° some trouble was caused by the interaction of the magnesia and carbon with the production of a dark grey sublimate. This, however, was not sufficiently energetic to materially interfere with the observations of the metal surface except at the high ebullition temperature of iron. The metals studied in this way were aluminium, chromium, iron, and manganese. It was early suspected that the boiling-points of aluminium and manganese were considerably lower than the values usually assigned to them, many circumstances pointing to this conclusion. With aluminium an additional difficulty was encountered in the shape of the very tenacious surface film of oxide always present, this rendering the commencement of ebullition very sudden. Manganese and chromium do not show this behaviour, but many experiments proved failures on account of the corrosive action of the metal on the magnesia lining—the higher temperatures being, of course, partly responsible. At the very high temperature necessary to effect the ebullition of iron (about 2500°) the reaction between magnesia and carbon becomes very vigorous, making the observations of the metal surface somewhat difficult. In all successful experiments, *i.e.*, in which the brasque had remained intact, the metal was found to be almost carbon free after the experiments. It was ascertained that the error in temperature measurement, due to the layer of badly conducting magnesia, was negligible by control experiments with silver and copper in brasqued crucibles, the values for the boiling-points being practically the same as those indicated above.

The values found for these metals are given below.

Aluminium	1800° C.
Manganese	1900
Chromium	2200
Iron	2450

No previous direct determinations have been made for these metals. Wartenberg states the boiling-point of

aluminium to be over 2200°, while the deductions from Moissan's work are valueless, seeing that no precautions were taken to prevent carburisation.

PART III.—Experiments at Pressures other than Atmospheric.

In these experiments the same general methods were used and the furnaces were of the same type as those in the experiments already described, but modified to fit

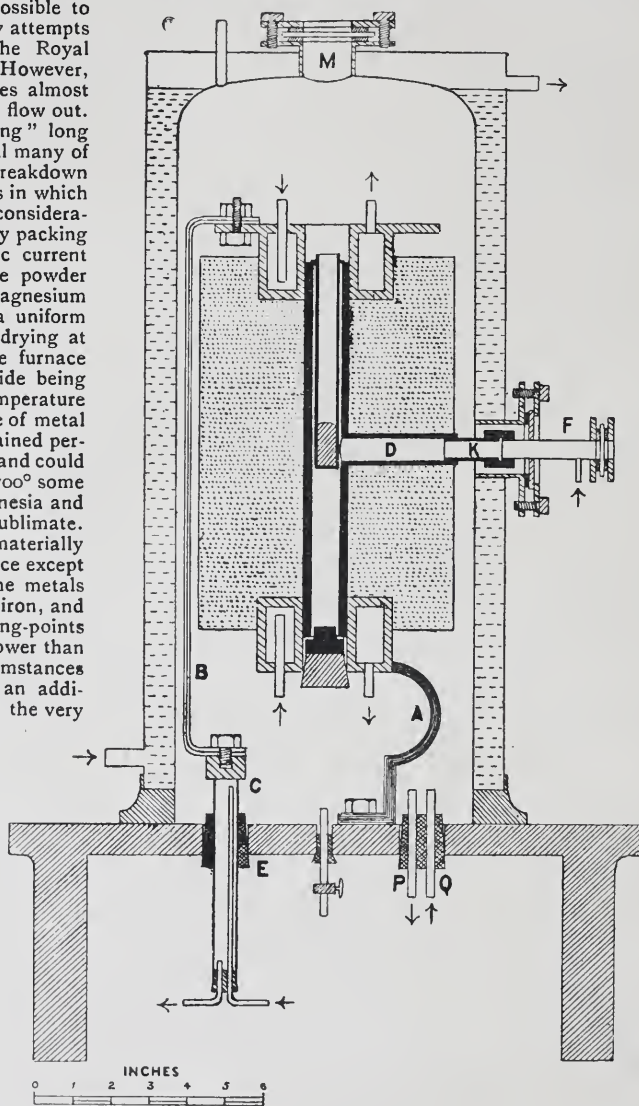


FIG. 3.

inside gas-tight enclosures. The form used for the experiments at reduced pressures is shown in Fig. 3. Here the furnace was arranged inside a water-jacketed tinned iron cylinder, mounted on a cast-iron ring, making an air-tight joint with the greased base plate. A resistor with water-cooled ends was used, water circulation being effected by P and Q. The current was led in by the water-cooled fitting C (insulated by the rubber stopper E) and the copper strips B, which were insulated by micanite ribbons and

* A Paper read before the Faraday Society, May 23, 1911.

returned through the copper spring A to the base plate. Observations of the metal surface were taken through the window M and temperature readings through the window in the fitting F. This fitting, which was fixed into but insulated from a graphite tube K, this in its turn fitting into the side tube of the furnace, was supplied with a slow current of nitrogen or hydrogen to ensure the absence of vapour in the sighting tube, and an air-tight joint to the body of the cylinder was secured by an asbestos washer. The evolution of occluded gas from the charcoal surrounding the resistor, together with the admission of gas at F, necessitated the employment of a powerful pump to maintain a constant vacuum. It was found easily possible, however, to keep down the pressure to below 10 cm. of mercury. The furnace resistor tube was of 20 mm. internal diameter and 20 cm. in length, and a current of about 350 amperes at 6 volts was required to attain a temperature of 2100°C . At reduced pressures the various stages of the ebullition were indicated somewhat more sharply than at atmospheric, and the effect of the gas in the side tube was found to be much less marked, hydrogen and nitrogen, for instance, giving almost identical results. This may probably be explained by the greater ease with

for the resistance furnace (*Phil. Trans.*, A, ccvii., 421). This consists briefly of a forged-steel cylinder (Fig. 5) provided with a lid, making a gas-tight lead spigot joint. Water-cooled electrodes pass through stuffing boxes at top and bottom, while various openings are provided for valves, windows, gauge connections, &c. It was difficult in this case to employ the ordinary water-cooled electrodes, so large graphite blocks were substituted, one being electro-coppered and soldered into the fitting carried by the water-cooled electrode F, while the other was held by stout steel strips connected to the cast-iron protection liner. By means of brass wedges this liner was put into good electrical contact with the main forging of the pressure enclosure and served as the return path for the current. It was possible to view the surface of the metal from a thick conical window A cemented into a steel cover. Temperature readings were taken through a similar window B fixed into a gun-metal fitting provided with a side tube C, which was connected to a cylinder of compressed hydrogen. (This gas, as well as that employed for obtaining the desired working pressure, was generated from zinc and sulphuric acid and compressed into cylinders; cf., Hutton and Petavel, *Journ. Soc. Chem. Ind.*, 1904, xxiii., 87). A

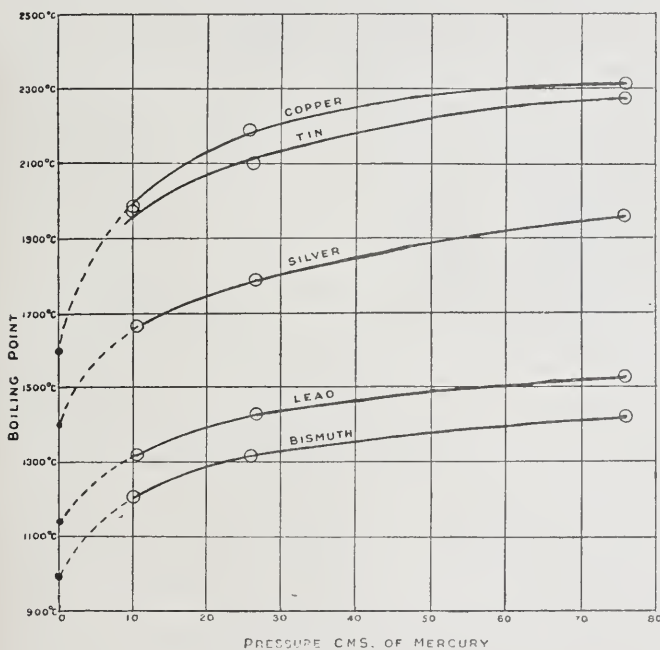


FIG. 4.

which hydrogen would diffuse through the crucible walls into the column of metallic vapour at higher pressures. The results of these experiments are given in Fig. 4 in graphical form—only metals unaffected by carbon being studied (the values for zero pressure are taken from the above-cited paper by Krafft—those for silver and copper being only probable estimates).

From these curves it may be seen that the metals in question conform fairly closely to Ramsay and Young's law in being similarly affected by pressure. It is consequently not unwarrantable to suppose that the boiling-points of the readily carburisable metals would show a closely similar dependency on pressure.

In addition to the experiments at low pressures, boiling-point determinations were also made at positive pressures ranging from 5 to 50 atmospheres, the high-pressure furnace designed by Dr. Hutton and Prof Petavel and already described by them being utilised as a containing envelope

current of compressed gas could thus be passed down the side tube of the furnace, and in practice no difficulty was experienced in keeping the tube free from fumes except in working at the highest pressures employed, when a rapid current of gas was required. The pyrometer was not sighted directly down the side tube, but the radiation was reflected from a plane mirror inclined at 45° to the axes of the tube and the pyrometer respectively, the correction for the loss on reflexion being determined by separate experiments. It was found unnecessary to fill the furnace to the full pressure at which it was desired to operate, for if about two-thirds of this amount of gas were introduced and the valves closed, the pressure quickly rose by expansion and disengagement of gas from the charcoal on commencement of the heating. Constancy was then maintained by allowing gas to slowly escape. The energy required in this furnace was a little greater than in the other forms—a current of about 600 amperes at 18 volts giving a temperature of 2000° . In the first experiments under pressure considerable trouble was caused by a curious convection effect in the column of compressed gas below the window A and through which the visual observations of the metal surface were taken. The pronounced wavering appearance set up made it extremely difficult to decide when the surface of the metal began to show a movement. This effect (which was absent at ordinary pressure) was finally almost eliminated by the

addition of a "chimney" E consisting of a carbon tube. With this arrangement the convection currents were almost entirely absent except with pressures above 50 atmospheres.

With regard to the sharpness of the observations this, as would be expected, was not quite so great as at atmospheric pressure. Sublimation below the boiling-point also seemed to be more pronounced, the clouds of vapour obscuring the metal surface to some extent. It was, notwithstanding, fairly easy to decide upon the point at which globules began to be thrown up. On account of the rapid rise of the boiling-point with pressure it was impracticable to study very high boiling-points (e.g., copper, boiling-point under atmospheric pressure 2310°) under pressure. With a metal of relatively low boiling-point like zinc the temperature-pressure curve was followed much further—up to 50 atmospheres. Above this pressure the convection currents and the dense clouds of vapour over the metal surface rendered observations very difficult. This

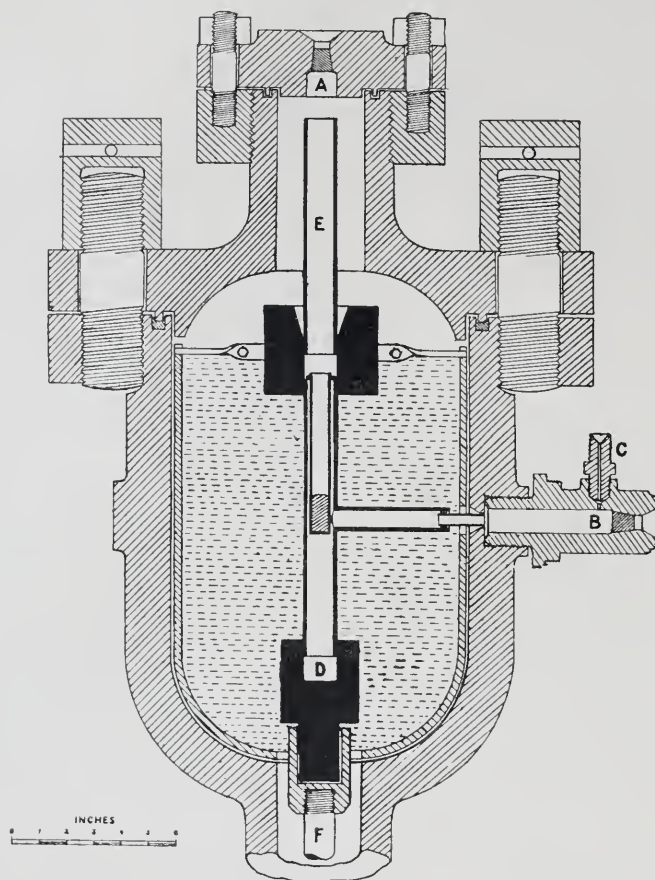


FIG. 5.

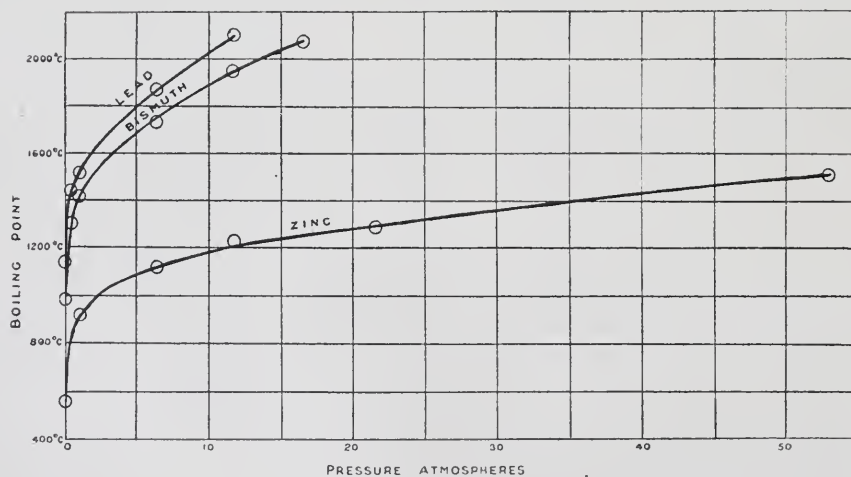


FIG. 6.

metal shows a somewhat abnormal behaviour, the character of the distillation, particularly at the higher pressures, having more the appearance of a very rapid volatilisation than of an actual ebullition. The results obtained with lead, bismuth, and zinc are expressed

graphically in Fig. 6. By comparison with Fig. 4 it will be seen how marked is the influence of pressure—the boiling-point of bismuth, for instance, being altered 860° within the limits of pressure used in these experiments.

APPENDIX.—Derivation of the Latent Heats of Vaporisation from the above Experimental Results.

In connection with the dependency of the boiling-points on the pressure it was thought of interest (*Zeit. Phys. Chemie*, 1911, [4], lxxvi., 484) to try to calculate the latent heats of vaporisation which are quite unknown quantities for these metals, except in the case of zinc.

Without entering here at length into thermodynamical considerations, we may obtain by integration of the equation—

$$RTd \cdot \ln p = Q \frac{dT}{T},$$

in which T represents the absolute temperature of the boiling-point, p the pressure in atmospheres, and Q the latent heat, assuming Q independent of T—

$$R \ln p = K - \frac{Q}{T}$$

or—

$$4571 \log p = K - \frac{Q}{T}.$$

The integration constant K, according to Trouton's rule, is universal, and may be obtained by dividing the absolute temperature of the boiling-point into the latent heat, its value being about 22. This rule, however, only holds for temperatures not very different from the ordinary temperature, and we find that a better agreement between theory and experiment is obtained by taking values of K greater than 22, this being particularly necessary with the metals of highest boiling-point. From such considerations the most probable values deduced for the latent heats are as follows:—

Metal.	Constant.	Latent heat.
Copper	27	70,600
Tin	29	73,900
Silver	25	55,800
Lead	25	45,500
Bismuth	25	42,700
Zinc	24	28,500

AN ELECTROLYTIC FURNACE METHOD FOR PRODUCING METALS.*

By JOHN WOODS BECKMAN.

AN electrolyte is generally understood to be a liquid which will conduct electricity, and the substances dissolved in this liquid are dissociated into two so-called ions. This was Arrhenius' theory, and has been applied ever since to water solutions. I believe though that O. Lehman and Lorenz and his co-workers are to be credited with having shown that the laws governing the water solution electrolyte are equally applicable to the molten electrolyte, and to substances dissolved in the same.

The above mentioned investigators have found and proved beyond a doubt that the substances dissolved in the molten electrolyte are ionised, and that the Arrhenius dissociation theory applies thereto; also that the laws governing the dissociation, the movement of the ions, and the speed of their movements, can be determined the same in molten as in water electrolytes. Lorenz in his classic "Die Electrolyse Geschmolzener Salze" has added through his painstaking work enormously to the knowledge of the fused electrolyte, the electrolyte of the future.

Up to the present time the industry which is making use of the molten electrolyte to the largest extent is the

aluminium industry. The ionic theory has long been applied to the reduction of aluminium from its oxide in the present well-known manner. Lorenz in the above-mentioned work publishes a very careful study made of the electrolytic deposition of aluminium from a molten electrolyte, and convincingly proves that it is an ionic reaction. His idea is confirmed by all who have studied the reaction and phenomena connected with the manufacture of aluminium; these phenomena are identical with those met with in plating copper from a copper-sulphate solution.

I once had occasion to do a considerable amount of work in connection with the manufacture of aluminium, and then appreciated the simpleness of the procedure. It should be possible to produce all metals in a similar manner from their oxides; but what electrolyte is to be used?

In the aluminium industry cryolite is used as a bath material; a mineral mined at considerable expense, and together with that of the other ingredients used in the electrolyte, its cost is considerable. The fusing point of this electrolyte is low, and it is on this account suitable for producing metals of low melting-points.

As a general law it can be considered that the electrolyte, fused or aqueous, from which a metal is to be produced, should be a solution containing in some form the desired metal. Cryolite, containing mainly the metals sodium and aluminium, is on this account not suitable as an electrolyte for the production of any other metal than aluminium.

When most salts are heated to their melting-point they dissociate, and this is especially the case with the salts of metals not belonging to the alkaline or the alkaline-earth metals. There are, however, exceptions among the heavy metal salts such as fuse but do not dissociate, and among these are the fluorides. Gin in his excellent monograph published in late issues of the *Transactions* of this Society, has outlined methods, using the double fluorides of various rare metals, and using these as fused electrolytes out of which to produce the desired metals. But these fluorides have to be produced artificially, and although the process seems perfectly feasible, the cost seems to be prohibitive to using these electrolytes commercially.

A comparatively little known group of salts are those occasionally occurring in nature, composed of equivalent amounts of calcium oxide and the oxide of any metal less positive than calcium. These salts occur occasionally in nature comparatively pure, as is the case with Scheelite, and can very readily be produced by heating the oxides together in any suitable manner.

It is evident that there is a great number of these salts possible, and the characteristic feature of them is that they all fuse at about and over 1000° C., the temperature varying according to the metal oxide which calcium-oxide is combined with. The boiling-point of these salts is very high; I have heated some to 2200° C., and the molten bath has been perfectly quiet, without any appreciable signs of the ingredients boiling off. The valuable feature of these salts, that I have availed myself of, is that when in a molten condition they carry the current very readily, and are very suitable as molten electrolytes for the production of a great number of metals. On a small scale I have produced a number of metals using the corresponding salt as an electrolyte. Manganese, iron, chromium, and a 50 per cent alloy of vanadium are the metals that I have produced so far. In the case of the alloy, it is interesting to note that it was produced as well out of the sulphide as out of the oxide. Crude ore was used, giving not a pure metal, but one containing some impurities such as silicon, unobjectionable as far as the steel trade goes.

The following gives in brief the procedure in manufacturing a metal by means of a fused electrolyte composed in the manner mentioned above. Take, for example, iron. Equivalent amounts of Fe_2O_3 and CaO are mixed together and heated in any suitable manner. The salt $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ is formed and fused in a receptacle fitted for electrolytic purposes. Oxide of iron is introduced into

* Paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 6-8, 1911. The author states that this paper is what might be termed "preliminary," and he hopes at a later meeting to be able to give some details which, in the present experimental stage of the process, would not now be advisable to offer. From the *Chemical Engineer*, xlii., No. 4.

this fused bath, and this molten solution is electrolysed, iron being deposited on the cathode, and a lively oxygen development taking place on the anode.

If the electrolyte itself is submitted to the direct current, no noticeable reaction takes place, but the moment iron oxide is added the electrolysis starts, and by adding from time to time more oxide it can be carried on continuously.

The actual intermolecular phenomena that do take place when electrolysis goes on are hard to define; there may be a continuous rearrangement of the salt structure, the iron oxide in the salt becomes detached, and another molecule of iron oxide takes its place, while the former is ionised, and gives off its electrical charges depositing iron and oxygen.

This method of producing metals is protected by patents in U.S.A. (U.S. Patent No. 973,336) and in other countries.

The practical features of this method are:—First, cost of electrolyte practically negligible, as it is composed of calcium oxide and the metal oxide of the desired metal; second, a great quantity of metal can be produced out of the same electrolyte; third, in case the electrolyte becomes fouled, the loss in discarding the electrolyte is practically negligible; fourth, the flexibility of the process, making it possible to produce a great number of metals and their alloys such as iron, manganese, chromium, zinc, tin, titanium, vanadium, tungsten, tantalum, molybdenum, nickel, cobalt, lead, and a number of others more or less rare.

In the following I am giving a list of amount of metal deposited per ampère-hour, considering only ideal conditions, and it is worth noticing, that aluminium has the minimum amount of metal deposited per ampère-hour, and is the only metal as yet that is produced commercially out of a fused electrolyte. Its use as a reducing agent for the production of many of the rare metals is well known.

Metal.	Oxide.	Grm. per amp.-hour.
Aluminium	Al ₂ O ₃	0.3377
Lead	PbO	3.868
Chromium	Cr ₂ O ₃	0.655
Iron	Fe ₂ O ₃	0.696
Manganese	MnO	1.027
Nickel	Ni ₂ O ₃	0.732
Zinc	ZnO	1.220
Titanium	TiO ₂	0.445
Vanadium	V ₂ O ₃	0.64

This process opens up a field which has heretofore been very little studied, and offers, I believe, a solution to many baffling electro-metallurgical problems.

REPORT ON METHOD OF DETERMINATION OF GLYCEROL.

By EUGENE PROBECK.

For some time chemists have failed to agree upon a standard method for the determination of glycerol. As the two methods most in use, the acetin and the bichromate, are fully described in many text-books, it is unnecessary to repeat them.

In the bichromate method, I did not remove the chlorine and albuminous matter as recommended by many chemists, but found it more advantageous to make a correction for these impurities by means of a blank test. This blank test depends upon the volatility of glycerol below 160° C., leaving behind the salts, polyglycerols, albuminous matter, and other organic impurities which do not volatilise.

Preliminary Test.—I weighed out about 2 grms. of the sample, diluted it to 200 cc., and tested 20 cc. of it for acidity, using phenolphthalein as an indicator. I found it took 2 drops of N/2 sodium hydroxide to neutralise the 20 cc. I added 2 drops to each 20 cc. I used for analysis,

and also added 2 drops to each 0.2 gm. of glycerin used for the blank test. The purpose of using an alkaline solution is to prevent any volatile acid from escaping by converting it into its sodium salt. If the glycerin is not neutralised in the blank test, the effect of the volatile acids on the bichromate solution cannot be determined.

The so-called blank test is made by evaporating about 0.2 gm. of neutralised glycerin on a watch-glass at 160° C. in a manner similar to the carbonaceous test given by Lewkowitsch in his "Technology of Fats, Oils, and Waxes." The residue is oxidised with the bichromate solution at the same time that the glycerin is. To prevent overheating and be certain of complete oxidation, both the residue and glycerin are heated on the same water-bath from one and a-half to two hours. The number of cc. of bichromate solution used to oxidise the residue is deducted from the number of cc. used from the sample, and from the difference the per cent of glycerol is calculated. The blank test makes a correction for all impurities likely to be present except volatile monohydric and dihydric alcohols and volatile aldehydes, chiefly acrolein.

I tested the glycerin with an ammoniacal silver nitrate solution but no silver mirror appeared, proving absence of aldehyde. If aldehydes are present, they must be removed, or the acetin method must be used. Experiments were made to find out the conditions under which acrolein is formed. I heated some crude glycerin to 160° C. as quickly as possible and then to 200° C. and no odour of acrolein was noticeable.

Carbonaceous tests have also been made to find out first, the effect of temperature on the glycerin, and second, the effect of sodium chloride on glycerin when heated. For convenience and clearness, it is well to divide the work into five parts:

I. Two carbonaceous tests were made of the crude glycerin, with these results: first trial 5.45 per cent, second trial 5.50 per cent.

II. A 100 cc. Florence flask was nearly filled with crude glycerin and heated as quickly as possible in an oven to 160° C. The glycerin was kept at this temperature for one hour and then two carbonaceous tests were made, with these results: first trial 5.50 per cent, second trial 5.50 per cent.

III. The Florence flask was refilled with fresh glycerin, heated as quickly as possible to 200° C., and was kept at this temperature two hours. The carbonaceous tests made with this glycerin gave nearly the same results as in the first two cases, indicating that the glycerin can be heated to 200° C. without polymerisation or decomposition. The results were: first trial 5.54 per cent, second trial 5.60 per cent.

IV. A fresh portion of glycerin was treated in the same manner as above except that the temperature was raised as quickly as possible to 250° C. and kept at 250° C. for two hours. The carbonaceous tests gave much higher results, as shown. First trial 12.60 per cent, second trial 12.50 per cent. These results indicate that glycerin cannot be heated to 250° C. without decomposition, polymerisation, or both.

V. Another Florence flask was nearly filled with crude glycerin and considerable sodium chloride was added. The glycerin was treated in the same way as in IV. The carbonaceous tests gave these results: first trial 8.80 per cent, second trial 9.01 per cent. The presence of salt in this case seems to retard the formation of polyglycerols. Sodium chloride was used because it occurs in soap lye glycerin, and it has been claimed that salts in glycerin interfere with the bichromate method.

The object of making so many carbonaceous tests is to show that the blank test can be used to advantage in determining glycerol in both candle glycerin and soap-lye glycerin. In case volatile monohydric and dihydric alcohols are present, both the acetin and bichromate methods are unreliable, as these alcohols are capable of being converted into acetyl compounds in the first method and capable of being oxidised in the second.

To show how accurate each method is, I made duplicate analyses of a crude glycerin with the following results :—

	Acetin method.	Bichromate method.
	Per cent.	Per cent.
First trial	86.08	86.93
Second trial	86.56	87.27
Average	86.32	87.10
Blank test correction		0.30
Corrected result ..		86.80

Conclusion.

From my experience with the acetin method, I conclude that no matter how carefully the method is carried out, the results are from 0.2 per cent to 0.5 per cent below the true value. The difficulty with the method is not on account of the impurities but on account of the manipulations introducing several sources of errors.

The bichromate method is preferable in the absence of acrolein and other volatile aldehydes. If aldehydes are present, they must be removed before using the bichromate solution. A blank test simplifies the method and makes the result more accurate than by purifying the glycerin.—*Journal of Industrial and Engineering Chemistry*, iii., No. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

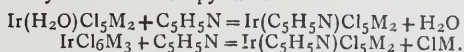
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 21, May 22, 1911.

Luminescent Neon Tubes.—Georges Claude.—In luminescent neon tubes the electrodes volatilise very rapidly. A deposit forms on the glass in their neighbourhood, and when it is treated with nitric acid a gaseous residue, insoluble in acids, is always obtained. This residue gives the helium spectrum. To prevent the volatilisation of the electrodes they must be made as large as possible, i.e., about 5 sq. dm. per ampère.

Radiation of Rubidium.—E. Henriot.—Rubidium emits a radiation giving a current of 3.64×10^{-13} amp. per 971 sq. cm. of surface of rubidium sulphate, while in the same circumstances the radiation of potassium is only 2.74×10^{-13} amp. The rays are more intense, but much more penetrating than those of potassium. There is a fairly good proportionality between the radiation and the percentage of rubidium.

Pyridine Pentachloro-iridites.—Marcel Delépine.—The pyridine pentachloro-iridites can be formed by replacing the molecule of water of the aquapentachloro-iridites or a molecule of alkali chloride of the hexachloro-iridites by a molecule of pyridine.



Treated with chlorine, with nitric acid, or with aqua regia they lose an atom of metal, giving the pyridine pentachloro-iridates $\text{Ir}(\text{C}_5\text{H}_5\text{N})\text{Cl}_5\text{M}$. The alkaline iridites are very stable. They are dissolved by concentrated sulphuric acid at 100°.

Iridotetrachloro-oxalates and Tetrachloro-iridites.

—A. Duffour.—When neutral sodium oxalate is added to a warm solution of disodium chloro-iridate, $\text{IrCl}_6\text{Na}_2.6\text{H}_2\text{O}$, effervescence occurs, and the liquid turns red, an aqueous solution of trisodic iridotetrachloroxalate being formed. $2\text{IrCl}_6\text{Na}_2 + 3\text{C}_2\text{O}_4\text{Na}_2 = 2\text{IrCl}_4(\text{C}_2\text{O}_4)_3\text{Na}_3 + 4\text{NaCl} + 2\text{CO}_2$. The potassium salt is readily obtained from the sodium

compound, and from the cold solution of the former the chestnut coloured silver salt is precipitated by the addition of silver nitrate. From the silver salt the corresponding acid $\text{IrCl}_4(\text{C}_2\text{O}_4)_3\text{H}_3$ can be obtained by the action of cold dilute hydrochloric acid. It is a very unstable acid and readily decomposes according to the equation $\text{IrCl}_4(\text{C}_2\text{O}_4)_3\text{H}_3 = \text{C}_2\text{O}_4\text{H}_2 + \text{IrCl}_4\text{H}$.

Phosphates of Uranyl and Amines.—L. Barthe.—By saturating an aqueous solution of orthophosphoric acid with a large excess of amine and adding a solution of uranium acetate the very stable compounds of uranyl and methylamine, &c., can be obtained. The author has prepared thus the phosphate of uranyl and methylamine, $\text{CH}_3\text{NH}_3\text{UOPO}_4$, the phosphate of uranyl and ethylamine, $\text{C}_2\text{H}_5\text{NH}_3\text{UO}_2\text{PO}_4$, and that of uranyl and trimethylamine, $(\text{CH}_3)_3\text{NHUO}_2\text{PO}_4$.

Action of Alkalis on Chloraloses.—M. Hanriot and A. Kling.—An aqueous solution of potash or soda turns a chloralose brown and a substance of formula $\text{C}_7\text{H}_{11}\text{O}_6\text{CHCl}_2$ is obtained. On hydrolysis this substance, which may be called dichloro-*p*-chloralose, decomposes into dichloraldehyde and glucose, $\text{C}_8\text{H}_{12}\text{Cl}_2\text{O}_6 + \text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_2\text{H}_2\text{Cl}_2\text{O}$.

Action of Methylene Chloride on Para-para-ditolylmethane.—James Lavaux.—When methylene chloride acts on *pp*-ditolyl methane in presence of aluminium chloride the two dimethyl anthracenes 1 : 6 and 2 : 7 are obtained. In order to produce the first substance the aluminium chloride has to effect an important molecular transposition.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 8, 1911.

Titration of Ferrous Oxide in Silicates by Pebal-Dölter's Method.—M. Dittrich.—When the iron in silicates is determined by Pebal-Dölter's method, after opening up with hydrofluoric acid and sulphuric acid, it often happens that the process is not complete but some silicate remains unchanged, and has to be treated with stronger sulphuric acid at a higher temperature before it dissolves. This is always the case with minerals and rocks that are strongly basic, poor in silicic acid, and rich in magnesia, and may be avoided by mixing the powdered mineral with quartz which has been not too finely ground.

Nitrate and Nitrite Assimilation.—Oskar Baudisch.—By the action of light the nitrosyl group can be formed from nitrates and nitrites. Thus, if an aqueous solution of potassium nitrite containing excess of methyl alcohol is exposed to ultra-violet light, oxygen is set free and oxidises the methyl alcohol to formaldehyde. This reacts in the nascent state with the nitrosyl potassium group, >NOK , and gives formhydroxamic acid, $\text{OHC} \begin{smallmatrix} \text{H} \\ \text{NOK} \end{smallmatrix}$. Ethyl alcohol behaves similarly. The reduction of nitrates and nitrites in presence of alcohols is purely a photo-chemical process, and does not take place in the dark.

Influence of Foreign Substances on the Activity of Catalysts.—C. Paal.—The addition of a metallic powder to palladium has a considerable effect upon its catalysing power. Thus Al, Fe, Cu, Zn, Ag, Sn, and Pb act as anticatalysers, while Mg, Co, and Ni have no effect. The action of the catalysts was tested with unsaturated esters. If benzene or acetone is used as solvent palladised nickel powder is rendered inactive, while ether and alcohol have no effect on the catalytic action when used as solvents.

Condensations by Ultra-violet Light.—Richard Pribram and Adolf Franke.—When the light from a quartz mercury lamp acts on aqueous solutions of formaldehyde it makes them condense, giving rise to a product which in some respects resembles glycol aldehyde.

Complex Mercury Compounds of Cinnamic Acid Ester and Cinnamic Acid.—Walther Schrauth, Walter Schoeller, and Richard Struensee.—When cinnamic acid esters and mercury acetate react in ethyl, propyl, isopropyl,

or isobutyl alcohol, complex mercury compounds are formed analogous to the α -mercury acetate β -phenyl methyl ethyl hydracrylic acid methyl ester already obtained from methyl alcohol. With cinnamic acid allyl ester the chloride—



is obtained. By the action of excess of potassium iodide solution on the anhydride of α -mercury- β -phenyl methyl ether hydracrylic acid, a substance which belongs to the class of α -mercury dicarboric acids is prepared.

Colour and Constitution.—Br. Pawlewski.—The author condensed the three amidobenzoic acids to form the nine nitrobenzalamido benzoic acids, which contain the solid chromophor group, $\text{N} : \text{CH}$, between two benzene nuclei, while the auxochrom carboxyl group and the second chromophor group NO_2 occupy different positions. In the derivatives of anthranilic acid the colour is deeper the nearer the auxochrom and chromophor groups are to one another, while in the derivatives of the other two amido benzoic acids the coloured compounds are those in which the CO_2H and nitro groups are furthest apart.

Aldehyde Hydrazine.—R. Stollé.—The addition of one molecule of hydrazine hydrate to one molecule of acetaldehyde in a little alcohol gives colourless crystals of aldehyde hydrazine, analogous to aldehyde ammonia. It melts at 60° , and is readily soluble in cold alcohol and water, and slightly soluble in ether and benzene. The faintly acid aqueous solution gives benzalazine when shaken with benzaldehyde. Aldehyde hydrazine is stable towards alkalis. No sodazide is formed when the alcoholic solution is heated with amyl nitrite and sodium ethylate. With silver nitrate in aqueous alcoholic solution it gives a white unstable precipitate of the silver nitrate double compound $\text{C}_6\text{H}_5\text{N}_6\cdot 3\text{AgNO}_3$, which apparently contains some water. On warming reduction occurs.

Zeitschrift für Anorganische Chemie.
Vol. lxx., No. 4, 1911.

Fusion Experiments with Bisilicates.—P. Lebedew.—The author gives the results of melting-point determinations with the systems CaSiO_3 — CaS , MgSiO_3 — MnSiO_3 , CaSiO_3 — BaSiO_3 , and BaSiO_3 — MnSiO_3 , and describes the optical examination of the melts under the microscope. Barium and calcium silicates are isomorphous with one another, as are also those of manganese and calcium.

Revision of the Atomic Weight of Iron.—Gregory Paul Baxter, Thorbergur Thorvaldson, and Victor Cobb.—The authors have worked out a new method of preparing very pure ferrous bromide by dissolving pure iron in a solution of hydrobromic acid of constant boiling-point, and drying the salt by heating it in a current of nitrogen and hydrobromic acid gas. The bromine in the bromide was determined by precipitating as silver bromide. The result obtained was $\text{Fe} = 55\cdot838$, if $\text{Ag} = 107\cdot880$, or $\text{Fe} = 55\cdot833$ if $\text{Ag} = 107\cdot870$.

Atomic Weight of Meteoric Iron.—Gregory Paul Baxter and Thorbergur Thorvaldson.—The method of determining the atomic weight of iron described in the preceding paper was applied to specimens of meteoric iron, when the mean results obtained in two series of experiments were $55\cdot837$ and $55\cdot835$. Thus there seems to be no reason for supposing that there is any difference between meteoric iron and the ordinary metal.

Sensitiveness of the Colorimetric Determination of Titanium.—Roger C. Wells.—The accuracy of the colorimetric determination of titanium is practically constant at concentrations which do not exceed at the most 1.5 mgrms. of TiO_2 in 100 cc. The alteration in concentration which is necessary in order to show an appreciable difference between two solutions amounts to about 6.5 per cent, a value which does not differ much from that found by the author for chromium and copper solutions. If suitable

precautions are taken the accuracy of the colorimetric method seems to be about 2 per cent.

Separation and Determination of Barium in Presence of Calcium and Magnesium by the Action of Acetyl Chloride in Acetone on the Mixed Chlorides.

—F. A. Gooch and C. N. Boynton.—When a mixture of acetone and acetyl chloride in the proportion of 4 : 1 is added to a very concentrated solution of barium chloride in water the water is decomposed. Hydrochloric acid is evolved and precipitation begins, and if the temperature is kept low all the barium is precipitated. The precipitate consists of the hydrated chloride $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$. By this method barium can be separated from calcium and magnesium, but not from strontium.

Action of Sulphuryl and Thionyl Chlorides on Tellurium.—Bela von Horvath.—Sulphuryl chloride acts on tellurium on heating in a dry indifferent atmosphere giving tellurium tetrachloride, $\text{Te} + 2\text{SO}_2\text{Cl}_2 = \text{TeCl}_4 + 2\text{SO}_2$. The action of thionyl chloride is represented by the equation $\text{Te} + 2\text{SOCl}_2 = \text{TeCl}_4 + \text{S} + \text{SO}_2$.

Halogen Aurates of Ethylene and Propylene Diammonium.—A. Gutbier and C. J. Obermaier.—To prepare the chloro- and bromoaurates of ethylene and propylene diammonium the dissolved ammonium haloid is added to the aurihalogen solution, and the precipitate is re-crystallised from the corresponding halogen acid. The compounds are stable in air, and relatively soluble in hydrogen haloid. Their formulæ are $[\text{C}_2\text{H}_4\cdot\text{N}_2\text{H}_6]_2\text{2AuCl}_4\cdot 2\text{H}_2\text{O}$, $[\text{C}_3\text{H}_7\cdot\text{N}_2\text{H}_6]_2\text{2AuCl}_4\cdot 2\text{H}_2\text{O}$.

Constitution of Metatungstates and Tungstic Acid Borates.—Arthur Rosenheim.—The author brings forward evidence to show that the formulæ ascribed by Copaux to heteropoly salts and by analogy to metatungstates are incorrect, and he adheres to his statement that the r_4 -tungstic acid borates do not exist, and that Werner-Miolati's hypothesis as applied to the heteropoly acids is correct.

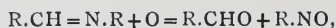
Atti della Reale Accademia dei Lincei.
Vol. xx., No. 8, 1911.

Researches on the N-Phenyl Ethers of Oximes.—A. Angeli, L. Alessandri, and M. Aiazzi-Mancini.—The N-alkyl ethers of the oximes which are formed when alkyl iodides condense with oximes, or when aldehyde condensates with substituted hydroxylamines, have been supposed to have the formula

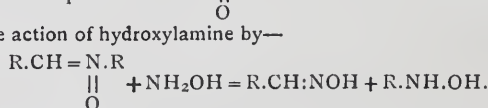


does not explain the instability of the substances towards permanganate, nor is it in agreement with the fact that in all reactions the oxygen never seems to be united with the carbon, but always with the nitrogen. Hence the formula $\text{R}\cdot\text{CH}=\text{N}\cdot\text{R}$

seems preferable. Then oxidation is shown



by the equation



the action of hydroxylamine by—

Arsenides of Tin.—N. Parravano and P. de Cesaris.—The fusion curves of mixtures of arsenic and tin indicate a eutectic at 228° , corresponding to 70 per cent of tin, and at 575° corresponding to about 61 per cent of tin. These two eutectics correspond to substances of formula Sn_3As_2 and SnAs .

Binary Systems : CuCl—AgCl, CuCl—NaCl, CuCl—KCl.—P. de Cesaris.—The system CuCl — AgCl has a eutectic corresponding to 44 per cent CuCl . CuCl — NaCl gives a eutectic at about 18 per cent NaCl , while in the system CuCl — KCl a compound $\text{CuCl}_2\cdot 2\text{KCl}$, as Sandonnini has shown.

THE CHEMICAL NEWS.

VOL. CIV., No. 2697.

THE DEVELOPMENT OF THE ATOMIC THEORY.* VII. THE RIVAL CLAIMS OF WILLIAM HIGGINS AND JOHN DALTON.

By ANDREW NORMAN MELDRUM, D.Sc.

THE rival claims of William Higgins and John Dalton to the atomic theory were much discussed early in the nineteenth century. The result of the discussion was, on the whole, favourable to Higgins. But from a variety of reasons, this result has been forgotten, and Dalton's claims are supposed at the present time to be beyond dispute. The author, in reviving the subject, hopes to present the facts, and to offer considerations, so as to enable anyone interested to come to a simple and fair conclusion upon it.

With the above purpose in view, it is necessary to consider the question, What is the essence of Dalton's atomic theory? This question, one of much interest, has proved, in the experience of writers on the subject, one also of much difficulty. An answer to it, which cannot be set aside, has recently been given by Larmor. In his Wilde Lecture—"On the Physical Aspects of the Atomic Theory"—he has expressed the Daltonian principle in the words "a definite molecule for each substance." He explains this more fully as follows:—"Perhaps the new feature developed by Dalton is at bottom describable as the principle of the essential homogeneity of each pure substance, that it is composed of molecules of only one type, absolutely alike. Once it is postulated that only one kind of aggregation into molecules occur, e.g., that in water there is only one way in which the hydrogen attaches itself to the oxygen, the laws of definite and multiple proportions are self-evident" (*Manchester Memoirs*, 1908, No. 10, lii., 9).

Undoubtedly this principle, "a definite molecule for each substance," is common to the various systems of chemistry of the nineteenth century. Yet the principle was not necessarily advanced first by Dalton. I have already shown (in the third paper of this series) that William Higgins expounded a definite chemical atomic theory in a book which he published in the year 1789. Further, the words, a "definite molecule for each substance," give, as will presently appear, an unexceptionable statement of the theory contained in Higgins' book.

The two theories, Higgins' and Dalton's, led their authors, in a remarkable degree, to the same results. This is proved by the following table, the formulæ in which reveal at once the ideas which Higgins and Dalton had regarding the molecules of the substances in question:—

	Higgins (1789).	Dalton (1803).
Water	HO	HO
Ammonia	—	HN
Oxides of sulphur ..	SO and SO ₂	SO and SO ₂
Oxides of carbon ..	—	CO and CO ₂
Oxides of nitrogen..	NO, NO ₂ , NO ₃ , NO ₄ , and NO ₅	N ₂ O, NO, and NO ₂

The great similarity between these results is to be explained in only one way. The two theories have in common, as a guiding principle, the rule that atoms of different kinds combine in the proportion 1 : 1 rather than in any other. It was this rule, and no other, which led each chemist to precisely the same conclusions regarding water, and the oxides of sulphur respectively.

How the rule was arrived at is a matter of the historical origin of the theories. As I have already shown, they

arose from the same central capital idea: Newton's postulate of "particles mutually repulsive" was the starting-point in each case. The thoughts of each chemist ran in the same groove. Similar particles repel one another, consequently particles of different kinds tend to unite in pairs.

Bryan Higgins was the first to reach this stage of thought, and he would not depart from it in any way. He supposed that the combination of one atom of alkali and two atoms of acid (or two of alkali and one of acid) must be prevented by the mutual repulsion of the two similar atoms, so that combination could not proceed further than 1 : 1.

Better acquainted than he with the facts of chemical combination, William Higgins imagined the combination of atoms in multiple proportion. But he laid it down that the combination in the proportion 1 : 1 was the most stable, thus adhering to the original idea of mutually repulsive particles.

The train of thought which Dalton followed had features of its own. His physical atomic theory was plainly an extension of Newton's, and was called for by the discovery of the existence of different gases, of their property of diffusing into one another, and of the properties of the resulting mixture. As I have shown in the fifth paper of this series, he held the physical theory for two years before he formed the chemical one. He was able to devise the latter in the space of a month, simply because he had the former to work upon.

The close resemblance between the two theories, both in principle and results, puts it beyond doubt that Dalton was forestalled by William Higgins. Humphry Davy, in his Bakerian Lecture of the year 1810, was the first to draw attention to Higgins' claims. The terms in which he did so are remarkably decided, and such as to throw him into almost too pronounced antagonism to Dalton. "In my last communication to the (Royal) Society, I have quoted Mr. Dalton as the original author of the hypothesis that water consists of 1 particle of oxygen and 1 of hydrogen, but I have since found that this opinion is advanced in a work published in 1789—'A Comparative View of the Phlogistic and Antiphlogistic Theories,' by William Higgins. In this elaborate and ingenious performance, Mr. Higgins has developed many happy sketches of the manner in which (on the corpuscular hypothesis) the particles or molecules of bodies may be conceived to combine; and some of his views, though formed at this early period of investigation, appear to me to be more defensible, assuming his data, than any which have been since advanced" (Bakerian Lecture, Nov. 15, 1810; *Phil. Trans.*, 1811, p. 15; Davy's Works, v., 326).

The only public notice which Dalton himself took of Davy's words was to publish a paper in which he was careful not to name Higgins. The date of Davy's lecture was November 15th, and of Dalton's paper December 19th. He contended that the use of the word *particle*, as opposed to *atom*, was a matter of great consequence—a contention which was quite unworthy of him (*Nicholson's Journ.*, 1811, xxviii., 81).

Though Davy saw fit afterwards to qualify this declaration, he could never undo the effect it produced. No one was better able than he to make Higgins known at once, for he was famous throughout Europe. His papers were read by all scientific men; thus Berzelius and Arago each mention that their attention was drawn to Higgins by Davy. The consequence in this country was a long and desultory controversy regarding the respective claims to the atomic theory of William Higgins and John Dalton.

In the course of the controversy the suggestion was made that Dalton had been guilty of plagiarism at the expense of Higgins. The charge was made far too lightly.* Dalton was not a great reader, and it was very

* Du Bois Reymond and Helmholtz each hit upon the same illustration of the time taken by a nervous impulse. "A whale probably feels a wound near its tail in about a second, and requires another second to send back orders to the tail to defend itself." "Hermann von Helmholtz," by von Königsberger, Eng. trans., 1906, p. 72.

* *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, lv., Part 2.

unlikely he would look twice at a book which dealt, on the face of it, expressly with the phlogiston controversy. But it was necessary that a statement on the subject should be made, and the statement was forthcoming. Thomas Thomson declared that Dalton had no knowledge of Higgins' book previous to the year 1810, and this declaration was made repeatedly afterwards by Dalton's personal friends (Thomson, *Annals of Phil.*, 1814, iv., 54; William Henry, "Elements of Experimental Chemistry," 1829, 11th edit., i., 45; W. C. Henry, "Memoirs of Dalton," pp. 78, 175, 217).

It is easy to account for the resemblance between the two theories. They had a common origin in Newton's ideas, and there is no need for any other explanation.

Thomas Thomson was Dalton's champion during the controversy, and he stoutly resisted Higgins' claims. The position he adopted is a specially interesting one. He declared that although Higgins' book had been widely read, no one had perceived the atomic theory in it. He therefore denied that the theory was there. This is not an answer, however, but an argument, and one that Thomson could hardly have used if he had kept in mind the reception Dalton's theory met with when it was launched upon the world (see the sixth paper of this series).

Humphry Davy, for instance, ignored it for long, and disparaged it when it was forced upon his notice. One can hardly wonder, then, that Higgins' speculations should have been disregarded, for they appeared many years before, under cover of a contribution to the phlogiston controversy.

Thomson, however, offered the testimony that he himself had failed to perceive the theory in Higgins' book. "I have certainly affirmed that what I consider as the atomic theory was not established in Mr. Higgins' book. . . . I have had that book in my possession since the year 1798, and had perused it carefully; yet I did not find anything in it which suggested to me the atomic theory. That a small hint would have been sufficient I think pretty clear from this, that I was forcibly struck with Mr. Dalton's statement in 1804, though it did not fill half an octavo page" (*Annals of Phil.*, 1814, iii., 331).

This is hardly enough to establish Thomson's case. It amounts to the plea that he was not making a mistake in the year 1814, simply because he could not have made it in the year 1798. Charles Darwin was a humbler man. As mentioned in the fifth paper of this series, he confessed that he and Sidgwick once passed along a valley without observing signs of glacial action, which were, none the less, present everywhere. They failed to perceive these signs because they were directing their attention to something else. In the same way the atomic theory may be in Higgins' book even though Thomson failed to perceive it.

As a result of the controversy, it appeared that most chemists were unable to deny Higgins' claims. William Hyde Wollaston observed that Mr. Higgins "in his conception of union by ultimate particles clearly preceded Mr. Dalton in his atomic views of chemical combination" (*Phil. Trans.*, 1814, p. 5). Thomas Graham, again, in his "Chemical Catechism," puts the question, "Who first made use of the atomic hypothesis in chemical reasonings?" The answer is:—"A. Mr. Higgins, of Dublin—in a book of his published in the year 1789" ("Chemical Catechism," 1829, p. 35).

Again, it is true that William Higgins has been almost forgotten. After his death, in 1825, he gradually passed out of notice and recollection. The claims of Dalton, on the other hand, have been advocated by a succession of Manchester chemists, including W. C. Henry, R. Angus Smith, and Roscoe and Schorlemmer. These writers have thought to advance their cause by disparaging Higgins, but, as I have shown in the third paper of this series, their criticisms are unfair, and must be set aside.

As I have already said, inasmuch as the "Daltonian principle, a definite molecule for each substance," is the

principle also of Higgins' theory of the year 1789, there is no avoiding the conclusion that Higgins forestalled Dalton. This is no small merit, for the said principle is the central idea of all the atomic weight systems of the nineteenth century.

It is, however, a great mistake to suppose that this conclusion exhausts the subject of the merits of the two chemists. Humphry Davy, years after his declaration on behalf of William Higgins, saw that there was something more to be said. He recognised the claims of Bryan Higgins:—"It is difficult not to allow the merits of prior conception, as well as of very ingenious illustration, to the elder writer" (Davy's Works, vii., 93). He said, further:—"Let the merit of discovery be bestowed where it is due, and Mr. Dalton will be still pre-eminent in the history of the theory of definite proportions" (*Op. cit.*, p. 96).

It is true on the one hand, that William Higgins was much indebted to Bryan Higgins, and on the other hand, that he left the atomic theory capable of infinite development by other chemists. It can be urged against him that he did not work out the practical consequences of his ideas. Why did he not make use of his ideas as a guide in experimental work? It might be supposed that he did not attach much importance to them, or he would surely have made strenuous exertions to establish them experimentally, and to make them known. But, as a matter of fact, there is nothing in his writings to show that he had anything but a high opinion of his theory. In the year 1799, seizing the opportunity of the publication of a book of his on bleaching, to draw attention to his system of chemistry, he declared that he had "connected the whole, and reduced it to a system, and made use of demonstrations which, in his opinion, are not to be invalidated or contradicted, until the order of natural things assume a different aspect" ("An Essay on the Theory of Bleaching," 1799, p. xx).

The strain of thought here is exalted enough to raise a smile, and, moreover, to prove the high value that Higgins set on his speculations. Elsewhere he stated that he taught the atomic theory in his lectures at the Royal Dublin Society. "What is called the atomic theory formed a part of my annual course of lectures" (*Phil. Mag.*, 1819, liii., 405).

Higgins thus exemplifies "faith without works." He had splendid ideas which he did not work out. More than one writer commented on this. Wollaston remarked that "he appears not to have taken much pains to ascertain the actual prevalence of that law of multiple proportions by which the atomic theory is best supported" (*Phil. Trans.*, 1814, p. 5). Davy, in his obituary notice of Higgins, passed a very severe judgment upon him: ". . . it is impossible not to regret that he did not establish principles which belong to the highest department of chemistry, and that he suffered so fertile and promising a field of science to be entirely cultivated by others; for though possessed of great means of improving chemistry, he did little or nothing during the last thirty years of his life" (Davy's Works, vii., 75).

William Higgins (saving his indebtedness to Bryan Higgins) stands in much the same relation to the chemical atomic theory as J. A. R. Newlands to the periodic system of the elements. Newlands foreshadowed the periodic system in its most important features. Although his ideas were scouted by the officials of the Chemical Society of London, he adhered to them, and was enabled to publish them by the open-mindedness of the Editor of the *CHEMICAL NEWS*. In Higgins' case, as in Newlands', we find an idea of extraordinary potency advanced by a man, who for some reason or other, leaves the idea almost in the germ and capable of infinite development by the efforts of others. Moreover, it was not through Higgins and Newlands that these ideas came to have an influence on the progress of science.

Granting the utmost that can be said on behalf of Higgins, one must admit that Dalton made a great contribution to the development of the atomic theory. Much

the superior of Higgins in energy of character and mind, he made himself a prime factor in the development of the theory by the persistency of his efforts to extend and apply it in all directions, and to bring it into currency amongst men of science. He applied it first to physical and then to chemical phenomena. In opposition to Berthollet's erroneous teaching regarding mixed gases and the composition of chemical substances, he offered sound ideas based on the theory. Again, he perceived, far more clearly than Higgins, the practical consequences of the combination of atoms. He never delayed putting his ideas to the test of experiment. The test was often hastily and crudely made, so urgently did he feel the necessity of making it. No one can say that the chemical atomic theory was accurately verified by Dalton, and no one can deny that his table of atomic weights brought the theory into touch with facts, and showed to all with eyes to see exactly what the theory meant. It has already been shown, in the sixth paper of the series, that Dalton converted Thomas Thomson to the theory, that Thomson influenced William Hyde Wollaston, and Amadeo Avogadro, and that Wollaston influenced J. J. Berzelius.

In preparing this series of papers, I made constant use of the "Royal Society Catalogue of Scientific Papers," and the "Select Bibliography of Chemistry," published by the Smithsonian Institution ("Smithsonian Miscellaneous Collections," Nos. 850, 1170, and 1440). On bringing the series to an end, I desire to acknowledge my indebtedness to the libraries of the following institutions:—The Victoria University of Manchester, Aberdeen University, The Manchester Literary and Philosophical Society, and The Glasgow and West of Scotland Technical College. At the same time I would tender my most grateful thanks to the respective librarians, Mr. Charles Leigh, Mr. P. J. Anderson, Mr. A. P. Hunt, and Mr. Peter Bennett, for the cordial way in which they facilitated my work.

RECENT ADVANCES IN HIGH-TEMPERATURE GAS THERMOMETRY.*

By ARTHUR L. DAY, Ph.D.

Director of the Geophysical Laboratory of the Carnegie Institute of Washington.

It is not the purpose of the present paper to discuss the general problem of thermometry, or the particular advantages of one system of thermometric measurement over another in laboratory or industrial practice, but merely to describe the work which has been done in recent years to increase the range and accuracy of the temperature scale upon which the various devices for measuring high temperatures depend for their calibration. Neither is it necessary to include any discussion of the relative theoretical merit or experimental practicability of the constant volume and constant pressure methods of gas thermometry. The reader will find it in Barus's review of the progress of pyrometry for the Paris Congress in 1900 (Carl Barus, "Les progrès de la Pyrométrie," *Rapports présentés au Congrès International de Physique*, 1900, i., 148), or in a more recent paper by Buckingham, of the American Bureau of Standards, as well as in earlier discussions to which they have referred. The choice of the one or the other method is likely to be governed by the taste or predilection rather than by the necessities of the individual experimenter. Neither system possesses decided advantages over the other. It happens that most of the recent measurements have been made with the constant-volume system.

The theoretical interest in gas thermometry centres about the quantitative relation existing between the increase in the temperature of the gas expanding under constant pressure or volume and the quantity of heat required to

produce it. It is a somewhat inaccessible question by reason of the difficulty of approaching it experimentally with the required accuracy. Although the amount of the expansion of gases is more closely proportional to the quantity of heat applied than that of liquids or solids, no strictly "perfect gas" in this sense has been found. The amount of the divergence between the expansion and the quantity of heat which produces it is slightly different with different gases, and also slightly different for the same gas at different temperatures. In the case of nitrogen, which has a greater range of practical utility than other gases thus far studied, the expansion curve diverges slowly from the regular curve of a perfect gas as the temperature increases, but the amount of its departure does not attain the magnitude of one degree Centigrade until the temperature reaches 1100° or more, and the uncertainty in this correction factor, if it is to be regarded as a correction factor, is probably smaller than the observation errors of an actual gas thermometer in the present stage of its development. For this reason, these theoretical considerations (which have been admirably treated by Buckingham in a paper "On the Establishment of the Thermodynamic Scale of Temperature by Means of the Constant Pressure Thermometer," *Bull. Bur. Standards*, 1907, iii., 237) do not seriously affect the definition of an accurate and practicable high-temperature scale by means of the gas laws.

On the other hand, there is no denying the fact that a great deal still remains to be done upon the experimental side before the steadily advancing requirements of both science and industry in the matter of a trustworthy temperature scale of sufficient accuracy, and even more particularly of sufficient range, can be satisfied. It is no disparagement of the present system of temperature definition to say that the gas thermometer itself is a complicated and cumbersome instrument to use in any of the forms which have hitherto been devised, and possesses limitations both of range and of accuracy which are difficult to overcome.

One consequence of this, particularly in the region of high-temperature measurements, is that temperatures easily come to be regarded with unwarranted confidence in the hands of those who have never acquired a first-hand knowledge of these limiting conditions. This has been sharply emphasised by the comparative ease with which relative measurements of temperature can be made, even in the more inaccessible parts of the scale, with the thermoelement and the resistance thermometer. These devices are sensitive to temperature differences of the order of magnitude of 0.01° throughout their entire range, but they are dependent absolutely upon fundamental measurements with the gas thermometer for their evaluation in terms of the generally accepted degree Centigrade. It is sufficiently obvious, though often carelessly overlooked, that no method of temperature measurement, however sensitive or adaptable it may be, can yield temperatures of greater absolute accuracy than the system in terms of which those temperatures are defined.

Another serious consequence results from the limitations of range of the gas thermometer in the region of high temperatures and the consequent temptation to extrapolation of a somewhat irresponsible kind. The highest temperatures (above 1600°) are conveniently accessible only to those methods of pyrometry which are derived from the Stefan and Wein-Planck relations, grouped together for convenience under the name "radiation pyrometers." These methods differ among themselves somewhat, both in principle and in application, but in general they are all characterised by common qualities. They do not require that the measuring instrument be in contact with the hot body, they are all comparatively convenient to use, and they may be said to have no upper temperature limit. These practical qualities are obviously of inestimable importance to all future pyrometric measurement, whether in laboratory or industrial work. Like all other pyrometers, however, they depend for their calibration upon

* A paper read before the Faraday Society, May 23, 1911.

the gas scale, and require to have their readings evaluated in terms of it.

Now it happens that these radiation pyrometers do not become effective as temperature-measuring instruments below a bright red heat corresponding to a temperature of perhaps 900° , and consequently they overlap the generally accepted Reichsanstalt gas scale for purposes of comparison and calibration only in the short interval lying beyond 900° and 1150° , beyond which the radiation scale both in the laboratory and in the shop is often extrapolated to 3000° or more, or about ten times the interval of measured temperatures. This is obviously very uncertain procedure, the more so perhaps because the radiation pyrometer is at its lowest sensibility in this 250° region in which the calibration requires to be made.

It is therefore clear that one needs not to go far beyond every day requirements in any branch of high-temperature activity to become keenly sensitive to limitations of an embarrassing kind. It would add immensely to the stability and trustworthiness of the radiation methods if the gas scale could be extended but two or three hundred degrees farther into the domain of radiation pyrometry. To be sure, we have the thermoelement which overlaps both regions—the gas thermometer from very low temperatures to 1150° and the radiation pyrometers from 900° to the melting-point of platinum (1755°)—but it also depends directly upon the gas scale, and its extrapolation beyond 1150° is fraught with equally grave uncertainty.

To meet this situation but four attempts have been made to measure temperatures above 1000° C. with the gas thermometer since the beginning of the present century. These may be taken up in order of their publication as follows: (1) J. A. Harker (1904) using a porcelain bulb and nitrogen; (2) Jacquerod and Perrot (1905) using a bulb of "quartz glass" and various gases; (3) Holborn and Valentiner (1906) using one bulb of platinum containing 20 per cent of iridium and one of pure iridium, both with nitrogen as the expanding gas; and finally (4) Day and Clement (1908) and Day and Sosman (1910) using nitrogen in bulbs of platinum containing 10 per cent of iridium and 20 per cent of rhodium respectively.

Harker, 1904.—The work of J. A. Harker at the National Physical Laboratory does not differ in any important particular from the work of Holborn and Day which immediately preceded it at the Reichsanstalt. His instrument was an exact duplicate of the Reichsanstalt instrument by the same maker (except that the bulb was of porcelain instead of platinum-iridium) and has since been altered only in certain minor particulars which need not be recounted here. His experimental operations were painstakingly performed, and the substantial agreement of his results with those of Holborn and Day affords valuable confirmation of the present Reichsanstalt Scale, but no attempt was made to extend its upper limit (1150°).

Jacquerod and Perrot, 1905.—Jacquerod and Perrot sought to establish a high-temperature scale from which two of the important sources of uncertainty in previous work should be eliminated: (1) the uncertainty due to differences in the expansion of the various available gases; (2) any uncertainty which might enter the problem through the expansion of the containing vessel (bulb). To accomplish the first object they prepared with the greatest care quantities of pure nitrogen, oxygen, air, carbon monoxide, and carbon dioxide, and used these successively for determinations of the melting-point of pure gold. To accomplish the second they selected for the material of their bulb a substance whose expansion coefficient was only about one-tenth as great as any which had been employed for the purpose up to that time. Both improvements afforded most valuable information. The five gases with appropriate corrections for their individual pressure coefficients gave the same temperature for gold within very narrow limits of experimental error, and the bulb proved impermeable to all the gases and of very low and regular expansion for the temperature range employed.

The relative accuracy of the individual measurements

with this system ($\pm 0.2^{\circ}$) was perhaps higher than has ever been attained with the gas thermometer at high temperatures, but the absolute temperature of the gold-melting point which they obtained (1067°) is considerably higher than any of the other recent measurements. Whether this is due to some inaccuracy in determining the constants of the (relatively large) unheated connecting space leading to the manometer, or to lack of uniformity in the temperature distribution about the bulb, or to insufficient data about the actual expansion coefficient of the quartz-glass bulb, or perhaps to an unfortunate combination of all of these sources of error, it is impossible for anyone except the experimenters themselves to determine. Certain it is that their work has contributed in two most important particulars to relieve the technique of gas-thermometry from the uncertainty which has hitherto surrounded it and has thus been of the greatest value to all who have followed or may follow Jacquerod and Perrot. Here again no effort was made to extend the fundamental measurements above 1150° , and the use of the silica bulb to which their success was mainly due definitely precluded such measurements with their system.

Holborn and Valentiner, 1906.—The experiments of Holborn and Valentiner contemplated a definite advance in this direction. Theirs was the first serious effort to extend the gas scale itself from 1150° , where all previous investigations had been halted, to 1600° C. The difficulties confronting such an undertaking are not only well known from earlier experience, but are of an insistent kind. Of the limited number of substances available for use as bulbs, none is without serious limitations at these extremely high temperatures; porcelain becomes soft and its walls both absorb and generate gas in prohibitive quantities; quartz glass devitrifies; pure platinum is very soft and is permeable to some gases; when stiffened with iridium or rhodium it is the best material available, but the iridium is destructive to the thermoelements, the bulb is likely to develop leaks and is permeable always to hydrogen if but a trace of the gas or of water vapour is about. Furthermore, the difficulty of maintaining a constant temperature about a bulb of 200 cc. capacity increases enormously at these temperatures, and the difficulty of measuring with thermoelements within the furnace is greatly increased by the conductivity of all insulating materials. It is also a matter of no inconsiderable difficulty to generate and regulate accurately the quantity of heat required for a bulb of this size under conditions where all electrical insulation begins to break down, and to protect the mercury manometer from so hot a furnace without removing it to an impracticable distance.

All these reasons, and others of inferior magnitude but often of exasperating pertinacity, contribute to the glory of Professor Holborn's splendid attempt to extend gas thermometry far out into this region, which had hitherto remained inaccessible to all the resources of the laboratory except the somewhat uncertain extrapolation methods. The bulb with which the highest temperature (1680°) was obtained was of pure iridium. It was small, only about 50 cc. in capacity, but held tight through several determinations of temperature reaching nearly to 1700° . The temperatures along the bulb were much less constant than for lower temperatures (differences of 60° on a bulb less than 10 cm. long), and many of the other difficulties noted above no doubt contributed something to influence the result, but the effort demonstrated beyond peradventure that the extension of the gas scale to 1600° is practicable.

Before turning to the present status of the experimental problem, which will carry us somewhat further into the consideration of details, permit me to say that I have omitted any mention of the beautiful work of Harker and Chappuis, or of Mr. Callendar and his associates, because it lies somewhat outside the scope of this enquiry. This work, most unfortunately, as it has always seemed to me, was confined to the temperature region below 500° , and so does not help us in the present situation.

By international agreement and nearly universal practice

two fixed temperatures are accepted as the basis of the modern temperature scale, the melting-point of pure ice and the boiling-point of pure water, both at normal atmospheric pressure (760 mm. of mercury). The interval included between these two temperatures is sub-divided into 100 parts by measuring the constant volume expansion of hydrogen from an initial pressure of 1 m. of mercury throughout this interval.

To extend the scale beyond these limits in either direction it is (theoretically) only necessary to continue the measurement of the expansion of hydrogen, under the same conditions, down to or up to any desired temperature. In practice this procedure encounters various experimental difficulties which increase rather rapidly as we get further away from the temperatures of everyday life.

These experimental difficulties serve to place definite limits upon the accuracy of temperature measurements at present attainable in different parts of the field of high temperatures, of which it is important to obtain a clear idea in order to be able to form a sound judgment of the probable significance of measurements at widely different temperatures. If we are told, for example, that a solution boils at $90^{\circ}27'$, we recognise that this accuracy is entirely practicable. If, on the other hand, platinum is said to melt at $1755^{\circ}46'$, it is of advantage to know that the last two figures are wholly without significance, and the fourth is uncertain.

There is another reason for being especially explicit upon this point, for very few investigators have ever made the laboratory acquaintance of the gas thermometer.

In its modern form the constant-volume instrument includes five principal features, which will be considered with particular reference to the limitations which they severally impose upon the accuracy of high-temperature measurements. The gas (1) is contained in an impervious vessel or bulb (2), which is heated in an electric furnace (3), arranged to provide the utmost attainable uniformity of temperature about the bulb at all temperatures. A mercury manometer (4) measures the gas pressure within the bulb, and thermo-elements (5) are used to transfer the gas-thermometer temperature to standard melting-points for general application. These will be briefly treated in order.

1. *The Gas*.—The first limitation to the upward extension of the gas scale is a direct result of the choice of a gas. Hydrogen was first chosen because it approximated more closely to a perfect gas in its behaviour than any other, but the experimental development of the subject has since demonstrated that no vessel can be depended upon to hold it without loss above 300° , so that nitrogen has come to be very generally substituted for hydrogen at the higher temperatures.

With reference to the situation created by this substitution, the long series of comparative measurements by Jacquero and Perrot (*Arch. d. Sci. Phys. et Nat. Geneve*, 1905, [4], xx., pp. 28, 128, 454, 506), using air, nitrogen, oxygen, carbon monoxide, and carbon dioxide, shows no measurable differences in the behaviour of these gases for thermometric purposes up to the melting temperature of pure gold (1062°), but some of these certainly could not be carried far beyond this temperature without danger of serious error through dissociation.

Nitrogen has been used, both in the Reichsanstalt and in the Geophysical Laboratory, as high as 1600° without any appearance of irregularity in its expansion or evidence of dissociation. The extension of the hydrogen scale by the use of nitrogen above 300° therefore encounters no serious difficulty up to the present limit of measurement (1600°) except in so far as it may prove necessary to make a small correction (of the order of magnitude of 1° at 1100°) for reference to the true thermodynamic scale if it is desirable to express the results of measurement in terms of it.

2. *The Bulb*.—The bulb is perhaps the most important single element in a constant-volume gas thermometer. The progress of gas thermometry during nearly a hundred years has been closely associated with and dependent

upon improvements in the bulb. The first bulbs were made of metal (Prinsep used a gold bulb in 1827), and there is little question to-day but that their abandonment for porcelain in 1857 (Deville and Troost) constituted a step backward which was not retrieved for forty years. The bulbs in use at the Reichsanstalt up to 1897 were still of porcelain, as were those used by Barus throughout his epoch-making work (Carl Barus, "On the Thermoelectric Measurement of High Temperatures," *Bull. U.S. Geol. Survey*, 54, 1888).

Porcelain, glazed or unglazed, violates both essential conditions for a good gas-thermometer bulb at high temperatures. (1) It cannot hold the expanding gas without absorbing or losing any of it; and (2) it is not absolutely uniform in its own expansion and contraction. Bulbs of platinum containing 10 to 20 per cent of iridium for additional stiffness were used at the Reichsanstalt in 1900 for temperatures as high as 1200° , and one of pure iridium was successfully carried to 1600° in 1907 . These bulbs are still in use.

The Geophysical Laboratory began its work with a 10 per cent platinum-iridium alloy, but abandoned it for platinum containing 20 per cent of rhodium, for reasons which will appear in connection with the use of thermo-elements below. All these metal bulbs can be used with nitrogen up to 1600° without appreciable error in the return to 0° after heating, provided only that proper precautions are taken against mechanical strain and consequent volume change at the higher temperatures where the metal is soft.

It is a matter of great difficulty and some uncertainty to make trustworthy measurements of temperatures above 1000° with platinum thermo-elements in the presence of iridium, even when the iridium is present only in a low percentage (0.005) alloy with platinum.

Parenthetically it may be remarked that the platinum crucibles and other ware as commonly made up for laboratory use are usually stiffened with from $\frac{1}{2}$ per cent to 2 per cent of iridium, a quantity amply sufficient to contaminate thermo-elements if they are exposed together to temperatures above 900° .

Porcelain bulbs when unglazed are not gas-tight; glazed within, they can be used up to 1100° without serious error, but the glaze becomes soft above this temperature, and reacts to some extent with the gas in the bulb, which then never returns to its initial pressure at 0° . Porcelain bulbs with outside glaze only were employed by Barus up to 1100° with fair success, but it proved impossible permanently to saturate the bulb wall with the gas, so that it would return to the same zero after heating. It is probable therefore that the porcelain bulb has permanently disappeared from gas thermometry.

Pure silica bulbs, which have recently been introduced by Jacquero and Perrot (*loc. cit.*, 1905), have an advantage over the metals, through their low expansion coefficient, but cannot be used above 1100° without permanent volume changes.

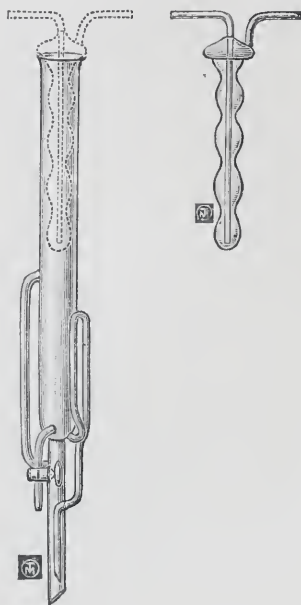
(To be continued).

Alloys of Molybdenum with Nickel, of Manganese with Thallium, and of Calcium with Magnesium, Thallium, Lead, Copper, and Silver.—N. Baar.—Molybdenum and nickel are completely miscible in the liquid state, but in the solid state they are miscible only if 0–33 per cent of molybdenum is present. They form a compound, $MbNi$. Manganese and thallium are miscible to a limited extent in both the liquid and crystalline states; in the liquid state at about 1200° , when 94.6–100 per cent of manganese is present, and in the crystalline state with 98–100 per cent of manganese. The avidity with which calcium reacts with the metals increases with the atomic weight of the metals. All the alloys of calcium investigated, except $CdCa$ and $AlCa$, are completely miscible. Extended series of mixed crystals seldom occur with calcium.—*Zeitschrift für Anorganische Chemie*, lxx., No. 4.

AN IMPROVED SOXHLET CONDENSER.

By OSWALD SILBERRAD, Ph.D.

THE object of this apparatus is to save all trouble in fitting up. Every chemist is familiar with the troublesome and unsatisfactory cork joint between the top of a Soxhlet extractor and the lower end of the reflux condenser attached thereto, to say nothing of the clamps, &c., required for supporting so cumbersome an arrangement. In



the present apparatus this is entirely done away with by simply inserting a bulbous Walters-condenser into the open end of the Soxhlet tube, somewhat lengthened for the purpose. The exact form of apparatus adopted, which may be procured from Messrs. Townson and Mercer, is shown in the accompanying diagram.

SOME NOTES ON THE SETTING OF CEMENT.

By W. A. B. WALLING.

DURING the course of some researches on cement it was found necessary to investigate a statement occurring in "Thorpe's Dictionary of Applied Chemistry," and some of the results obtained have an interesting bearing on this statement.

In Thorpe (vol. i., p. 477) some figures, relating to a cement manufactured from a stone quarried in the neighbourhood of Heidelberg, are given.

	Per cent.
CaO	44.22
MgO	17.77
Fe ₂ O ₃ and Al ₂ O ₃	8.82
Oxides of Mn	2.33
Alkalis	4.72
SiO ₂	22.14

Further, a good cement burnt at a high temperature contained 100(SiO₂:R₂O₃)₃₀₄(CaOMgO).

The following theories as to the setting of this cement are advanced in "Thorpe's Dictionary":—

1. When the stone is burnt at a low temperature, about 400° C., the MgO is rendered caustic and not the CaO, and the MgO acts as the hydraulic agent.

2. When burnt at a high temperature it almost fluxes, and the silicates of CaO and MgO formed act as the hydraulic agents.

Some silicates of magnesium were prepared, and the results of hydrating them are set forth in the following table:—

Mixture taken.	Clinker.
SiO ₂ + MgO	Fused and hard
SiO ₂ + 2MgO	Fused and hard
SiO ₂ + 3MgO	Softest of any
2SiO ₂ + MgO	Fused and hard
3SiO ₂ + 2MgO	Fused and hard
3SiO ₂ + 4MgO	Fused and hard

(No setting obtained in any member of series).

The above products were prepared from pure sand and pure magnesia, roasting at a high temperature, 1100° to 1500° C.

Using a high grade lightly calcined magnesite and Medway clay, in the proportions required to obtain silicates of magnesium, the following results were obtained:—

Silicate.	Clinker.
MgO.SiO ₂	Hard
2MgO.SiO ₂	Hard
3MgO.SiO ₂	Soft
MgO.2SiO ₂	Hard
2MgO.3SiO ₂	Hard
4MgO.3SiO ₂	Soft

(No setting obtained in any member of series).

The above were all roasted at a high temperature.

It seems more difficult to obtain silicates of magnesium from Medway clay used than from pure materials. The silicate SiO₂.3MgO was probably not obtained, as a glance at the table will show. Le Chatelier did not prepare this silicate, and the first two in the above table as obtained by him had no setting properties. Le Chatelier could not obtain the silicate SiO₂.3CaO. A microscopic examination of the clinker of the above silicates revealed in the case of all but SiO₂.3MgO, the presence of small plate-like crystals, and, in the first two, no free magnesia or silica, and only traces of these in the other hard clinkers. Thus a definite compound was probably obtained in each case.

From these experiments it is obvious that the silicates of magnesia, as obtained, have no setting properties on hydration.

A sample of magnesite, heated for five hours at 400° C., until no carbonate remained, did not set on hydration. Pure MgO did not set when similarly treated. Working on the formula 100(SiO₂.R₂O₃)₃₀₄.(CaOMgO), the experiments tabulated below were carried out at 1100° C. They were also conducted at 400° C., with similar results.

Materials.		Proportions.	Clinker.
Medway clay (wts.).	MgO (wts.).	SiO ₂ : MgO.	
6.03	16.30	1 : 3.04	Soft, white
6.03	10.66	1 : 2	Slightly harder
6.03	5.33	1 : 1	Same as above
9.65	5.33	1.6 : 1	Harder
12.06	5.33	2 : 1	Soft
18.33	5.33	3.04 : 1	Hard
9.65	8.53	1 : 1.6	Very hard

(No setting in any of these).

It was found that the addition of small quantities of CaO before roasting increased the cementitious tendencies of the cement. Setting properties increased with the lime present, and decreased with the magnesia. Others of the author's experiments undoubtedly prove this.

In the face of these experiments it seems more probable that the setting of the Heidelberg cement was due only to the silicate of calcium, and that the silicates of magnesium played no part—except, perhaps, to weaken the cement. Further, the author has been unable to obtain MgO that will set as stated in "Thorpe's Dictionary." What evidence is there in support of the setting properties of lightly calcined magnesia?

Battersea Polytechnic Research Laboratory,
July 3rd, 1911.

APPLICATIONS OF PHYSICAL CHEMISTRY TO THE DOCTRINE OF IMMUNITY. ANTIGENES AND ANTIBODIES.*

By Prof. SVANTE ARRHENIUS, D.Sc., Hon.F.R.S., Hon.F.C.S.
Director, Nobel Institute of Physical Chemistry.

(Concluded from p. 41).

IX. The Compound Hemolysins.

IN former times so-called "transfusion," *i.e.*, injection of animal blood in the veins of the patient, was often used to refresh the blood of patients suffering from different illnesses. This treatment was often found pernicious, because the foreign blood "killed" the human red blood-corpuscles. This noxious action is due to the serum of the animal blood. Only blood from the same species is harmless. Daremberg proved, in 1891, that the "globulicid" action of the foreign blood is lost if it is heated to 50–60° C.

In the same manner blood-serum is "bactericid," *i.e.*, it kills bacteria (Fodor, 1887). This "bactericid" property of the serum also vanishes after heating to 60° C. (Buchner).

In 1894, Pfeiffer found that the "bactericid" action of an animal's serum is increased in a very high degree if the animal receives injections of a suspension of the bacteria in question. This serum thereafter contains a bacteriolysin specific to the injected bacilli (Pfeiffer used cholera-vibrions). Bordet then proved that these hemo- and bacteriolysins are compound substances, consisting of one part, alexin, which is rapidly decomposed on heating to 55° (see above, VI.), and one part, the immune-body, which resists this high temperature. This immune-body is specific against the injected cells, and is absorbed by them in a very high degree (see above, VI.). It does not alone cause lysis; but after the addition of some alexin (guinea-pig serum is mostly used as alexin), it gives a strong lysis. Red blood-corpuscles, containing the immune-body, are therefore rapidly hemolysed if they are brought into a serum.

The serum containing the immune-body acts also by agglutinating red blood-corpuscles, against which it is specific. It has been much discussed whether this agglutinin is identical with the immune-body or not, and the same question has been raised regarding the bacteriolysins and accompanying agglutinins. The influence of foreign substances changes the two qualities in different proportions, and therefore it has been concluded that we have to deal with two different substances. As we have seen above, this conclusion is not very certain (see above, VIII.).

Bordet supposed that the immune-bodies act as sensibilisators. Ehrlich and his school held the opinion that a chemical compound of the immune-body and the alexin is formed, which has hemolytic properties. They further thought that this compound is bound to the red blood-corpuscle, which they treat as if it were a big molecule. This latter view seems very improbable; the fact is that the hemolytic molecule is formed within the blood-corpuscle, where it attacks some albuminous substances, and causes hemolysis, just in the same manner as do the simple hemolysins (*e.g.*, tetanolysin).

If Bordet is right, the hemolytic action would be proportional to the product of the added quantity of alexin and that of immune-body, or perhaps to some power of these quantities. This is really the case for the action of cobra-poison in presence of lecithin (see above, VII.), and therefore this case may be regarded as due to a sensibilising action of the lecithin. As a matter of fact, Ehrlich regarded this case as a typical paradigm for the binding of immune-body to alexin. In this special point he was not successful; but regarding the real immune-bodies and alexins his opinion was right. If we take a certain small quantity of alexin, and add it to a given quantity of red blood-corpuscles, we do not attain complete hemolysis,

even with very large quantities of immune-body. And, *vice versa*, if the quantity of immune-body is small, we shall not have complete hemolysis even with very great quantities of alexin. (It may here be said that the guinea-pig serum in itself contains a small part of hemolysin, so that it is necessary to correct for the action of this quantity). This indicates that a hemolytic compound is formed from the alexin and the immune-body; and if one of these is not present in sufficient quantity, then even the quantity of hemolysin will be insufficient, for it cannot exceed the quantity equivalent to the quantity present of that of the two components which is present in the least quantity.

I have investigated a considerable number of cases, varying the quantity of alexin and of immune-body, and have found that the quantity of hemolysin formed, as compared with the quantities of immune-body and of alexin, is subject to the law of chemical equilibrium. The results of the experiments could always be calculated in this way, so that there is no doubt that the hemolysin is an additional product of the alexin and the immune-body, and that these three substances are in equilibrium with each other. This equilibrium, so far as regards the hemolytic action, takes place in the interior of the blood-corpuscles.

As an instance of how well the law of chemical equilibrium agrees with the experiments regarding the production of hemolysin from immune-body and alexin, I give the following figures representing the degree of hemolysis produced on blood-corpuscles from an ox by a mixture of heated immune-serum (*a*) from a goat, injected with blood-corpuscles from the ox, and the alexin (*b*) of normal guinea-pig serum. The quantities *a* and *b* are expressed in cubic millimetres of the two sera. The figures given in brackets are calculated from the formula:—

$$(5a - x)(20b - x) = 90x.$$

x is the quantity of hemolysin. The degree of hemolysis is proportional to the square of the quantity of hemolysin. If the calculus gives a higher degree of hemolysis than 100, it corresponds to total hemolysis, and is represented in the table by the figure 100, which is the highest possible degree of hemolysis (expressed in per cent).

With small quantities (*a*) of immune-body even the tenfold quantity (*b*) of that quantity of alexin which is sufficient to produce total hemolysis does not give enough hemolysin to yield a hemolysis of more than about 40 per cent. The same is valid for the immune-body. If the quantity of alexin is very small, 0.6, we obtain not more than about 15 per cent of hemolysis. The added quantity (*a*) of immune-body may be as great as may be desired.

<i>b</i>	<i>a</i> =10.	<i>a</i> =30.	<i>a</i> =100.	<i>a</i> =300.	<i>a</i> =900.
60	40 (46)	—	—	—	—
40	37 (45)	—	—	—	—
25	38 (42)	—	—	—	—
15	39 (37)	—	—	—	—
10	38 (33)	71 (84)	98 (100)	100 (100)	—
6	22 (25)	59 (60)	85 (98)	98 (100)	—
4	20 (20)	45 (44)	75 (66)	82 (73)	—
2.5	—	27 (29)	51 (43)	47 (47)	—
1.5	—	15 (18)	25 (25)	22 (28)	24 (29)
1	—	—	15 (17)	15 (19)	18 (21)
0.6	—	—	11 (10)	13 (11)	13 (14)

Another experiment indicates that a similar equilibrium also takes place outside the blood-corpuscles. If we mix a certain quantity of alexin with different quantities of immune-body, and let the mixture remain for half-an-hour at 37° C., and thereafter let it act upon the corresponding blood-corpuscles, we find a maximum action at a certain medium concentration of the immune-body. This is explained in the following manner:—If no immune-body is present the action is zero, and it increases therefore, to begin with, with the quantity of immune-body used. The hemolysin formed is dissociated in a rather high degree, and the constituents alexin and immune-body diffuse into the red blood-corpuscles, and are absorbed there and form

* A Discourse delivered at the Royal Institution, June 9, 1911.

the hemolysin. If the immune-body is present in great excess the alexin is nearly wholly consumed for the formation of hemolysin, therefore it diffuses very slowly and in small quantities into the red blood-corpuscles, so that only insufficient quantities of hemolysin are formed in them. Of course new molecules of hemolysin dissociate and deliver new quantities of alexin, but this decomposition goes on rather slowly. Therefore during the time of action (two hours at 37° C.), the quantity of hemolysin formed in the blood-corpuscles is insufficient. Evidently there must be a maximum of action when the immune-body and the alexin are present in equivalent quantities, and that is really what has been found experimentally. This phenomenon, which has been called "diversion of the alexin," was found by Neisser and Wechsberg in investigations regarding bacteriolysins. The corresponding phenomenon with hemolysins was eagerly sought for but not found until I made some quantitative experiments with red blood-corpuscles from an ox, immune-serum from an injected rabbit, and guinea-pig-serum as alexin. It was not observed in other combinations investigated by me, and it is not very prominent, so that it was necessary to use quantitative measurements on the degree of hemolysis. The red blood-corpuscles were very carefully washed in 0.9 per cent sodium-chloride solution, and thereby freed from the accompanying serum. If that had not been the case the simultaneous injection of serum would have produced a formation of a precipitin (see below, X.) which, with the serum on the surface of the blood-corpuscles might have produced a precipitate, which has a great power for absorbing alexins, so that thereby the insufficiency of alexin, if a certain quantity of immune-serum was added, might be explained. As a matter of fact, Gay has made a similar objection to the experiments of Neisser and Wechsberg (see below, X.).

As stated above, Madsen and Teruchi observed the absorption of streptolysin in red blood-corpuscles at low temperatures (near 0° C.) without interference of hemolysis, notwithstanding that the absorbed quantity was much more than sufficient to produce total hemolysis. If these corpuscles, with their content of streptolysin, were heated to 37° C. for a quarter of an hour, they were totally hemolysed. Of course the lysin exists also at the low temperature, but the velocity of the reaction which causes hemolysis is extremely small at that low temperature and rather great at 37° C. The compound hemolysins behave in the same manner. There is still another circumstance. The immune-body is absorbed in a high degree, and very rapidly by the blood-corpuscles. On the other hand, most alexins do not seem to be absorbed in a high degree by blood-corpuscles if immune-body is not present in them to combine with them. According to experiments by Malvoz, alexin from dog-serum forms an exception. It is absorbed in a high degree by red blood-corpuscles from rabbits, for if they have been treated with dog's serum and then placed in a solution of the right immune-body, they become hemolysed. Now if we place sheep corpuscles in a mixture of immune-body from goat's serum and alexin (normal goat-serum), and let them remain in this mixture for some time at a low temperature, no sensible quantity of hemolysin is formed in the blood-corpuscles because of the very low velocity of reaction at that temperature (0 to 3° C.). But a great quantity of immune-body is absorbed. This is apparent from the fact that the blood-corpuscles are not subject to hemolysis if heated to 37° C. for one hour, but are hemolysed as soon as alexin is added. At 40° the experiment also succeeds, but only partially, if the corpuscles are separated from the mixture within ten minutes. Then a certain degree of hemolysis is observed which is increased in a high degree after addition of alexin (Ehrlich and Morgenroth). Evidently the whole phenomenon depends only upon the very slow reaction of hemolysin formation at low temperatures and the corresponding small absorption of alexin. Ten minutes at 40° C. correspond to about 400 minutes at 0° C., according to the general change of the velocity of reaction with temperature. The

conclusion of Ehrlich and Morgenroth that hemolysin, which is stable at 40°, should not be so at 0°, is extremely improbable.

X. The Precipitins.

Those organic substances which give a precipitate with some albuminous substances are called precipitins, e.g., rennet, precipitating casein from milk, is called a precipitin. But this name is often reserved for such precipitating substances as are specific and have been prepared by the injection of the albuminous substance in question into the veins of an animal. Thus, for instance, the blood-serum of animals injected with milk contains a precipitin against milk, called lactoserum, which, like rennet, precipitates casein. It has been studied carefully by Bordet and P. T. Müller.

Lactoserum is decomposed at about 70° C. As its compound with casein is partially dissociated, heating to 70° C. for a certain time decomposes the total quantity of the serum, so that the casein is regenerated. The process as regards casein is wholly reversible. Generally speaking, the processes investigated in immuno-chemistry are reversible, but the treated substances are so easily altered, like the lactoserum, that their composition is changed by secondary processes, and it is therefore in most cases impossible to recover them quantitatively.

If we add casein in increasing quantities to a given quantity of lactoserum, the precipitate increases to begin with, but is dissolved again later on. The precipitate, which is obtained by adding increasing quantities of egg-white to a given quantity of its precipitin, according to Eisenberg behaves in the same manner. Evidently we have to deal here with cases of chemical mass action analogous to those which we obtain when we add increasing quantities of an alkali to different salts of certain metals, such as zinc, lead, aluminium, &c., in which case we also at first obtain a precipitate, which later on becomes dissolved.

A special interest attaches to those precipitins which are obtained through the injection of the blood-serum from one animal into the veins of another. Their behaviour has been investigated quantitatively by Hamburger in Groningen. As an instance, I give the following figures of Hamburger, regarding immune serum from a rabbit injected with serum from a sheep. He mixed 0.4 cc. of the immune serum with different quantities A (in cc.) of sheep's serum (diluted with 49 parts of 0.9 per cent NaCl solution). After a while he determined the quantity P of precipitate by centrifuging it down into a narrow graduated tube. P is measured in units of 0.0004 cc. This quantity has been calculated by me according to the following formula:—

$$\frac{40A - P}{V} \cdot \frac{120 - P}{V} = 250.$$

This formula indicates that the precipitate is a compound of the two sera. Every cc. of the solution of sheep's serum is equivalent to 40 units of the precipitate, and the 0.4 cc. of the immune serum is equivalent to 120 units of the precipitate. If therefore P units of precipitate have been formed from a mixture of A cc. sheep's serum, i.e., 40 A equivalents, and 0.4 cc. immune serum, i.e., 120 equivalents, then there remain (40A - P) equivalents of the sheep's serum, and (120 - P) equivalents of the precipitin. If we divide these quantities by the volumes V, and form the product, as in the formula above, this product ought to be a constant, according to the law of Guldberg and Waage. The results are given in the accompanying table.

In the last three experiments 1 cc. of water was added to the mixture, whereby the volume V was increased, and consequently the precipitate diminished. The general agreement between the calculated and the observed quantities of precipitate shows that the remaining discrepancies (e.g., for A=1.5, 2, and 15 cc., as well as in the last two figures) may be supposed to be due to the great experimental difficulties inherent in these measurements. The constants 40, 120, and 250 are determined from the experiments.

Quantity A.		V ₂ (Cc.?).	Quantity of precipitate P.	
Cc.	Equiv.		Obs.	Calc.
0.02	0.8	0.162	1	0.5
0.04	1.6	0.163	2	1.3
0.1	4	0.25	3	3.5
0.15	6	0.302	6	5.3
0.2	8	0.36	7	7.2
0.6	24	1	21	21.5
1	40	1.96	35	34
1.5	60	3.61	39	48
2	80	5.76	60	57
3	120	11.56	67	66
5	200	29.2	64	65
7	280	57.8	58	58
10	400	108.2	49	46
15	600	237	10	19
18	720	338	5	3
20	800	416	2	0
1) +1	40	5.76	28	25
5) cc.	200	41	57	51
10) H ₂ O	400	130	41	32

In this case we observe an increase of the precipitate P when the quantity of added sheep's serum A increases. But a maximum is soon found, when A = 3 cc., and thereafter the precipitate decreases. The calculation indicates that this circumstance is only due to the increase in volume; that is, to the attenuation, whereby the concentration of the immune serum diminishes without a commensurate increase in the concentration of the sheep's serum.

But, as stated above, cases are not rare in which a real chemical action takes place between the precipitate already formed and the further addition of the antigen, whereby the precipitate becomes dissolved. Hamburger has given an example of this kind. It relates to serum from the horse, and immune serum, containing precipitin, from the calf. The horse serum was attenuated to a fiftieth, and 1 cc. of that preparation corresponded to three times the used quantity of calf's serum, namely, 1 cc., which is considered equal to 100; therefore 1 cc. of the diluted horse serum was considered equal to 300 in the formula for calculation. The maximum quantity of precipitate corresponded to 100 units, but in the experiments only 59 units were obtained, because the dilution was rather great. The results of these experiments are contained in the following table:—

Quantity of horse serum.	Quantity of precipitate.	
	Obs.	Calc.
4	0	0.2
8	3	3.9
15	10	10.3
24	17	17.8
30	21	23.6
39	32	29.7
45	34	34
54	43	40.1
60	45	43.9
75	52	51.9
79	51	53.6
88.3	55	57.1
90	57	57.5
100	59	58.9
115.4	55	57.4
137	50	51.3
167	43	41.3
214	25	26.8
300	5	5.5
500	2	0

Even in this case the observations agree well with the calculation. It must, however, be remembered that we have here four constants to determine experimentally, namely, the number of equivalents (counted in units of

precipitate) contained in 1 cc. of each of the two sera, and further two constants of equilibrium for the two compounds, the precipitate and its soluble compound with the albuminous substance in the horse serum. It is thereby possible to obtain a fairly good agreement, if the errors of observation are not too great.

The immune serum from a rabbit injected with sheep's serum gives a precipitate with the serum not only of sheep, but also of related animals, as goats or cows. In these cases the quantity of precipitate was less; instead of 300 units per cc. in the sheep's serum, the corresponding figures were, for the goat's serum 212, and for the serum of cows only 90. These figures indicate that sheep and goats are very nearly related, and in a much lesser degree related to cows. This method evidently gives a possibility of determining the relationship between different animals quantitatively. As is well known it has already been used for similar determinations, but only qualitatively.

In the early days of the development of the doctrine of immunity it appeared to be possible to prepare antibodies against antibodies themselves, which are all constituents of immune sera. Thus, for instance, Bashford prepared an antibody against antiricin, the so-called anti-antiricin. The school of Frankfort prepared anti-immune bodies and anti-alexins, and so on. Recent investigations make it probable that this new anti-action is due to a precipitin against the injected immune serum, which precipitin, when mixed with this immune serum, gives a precipitate. As is the case with many precipitates this carries down with itself the large part of the dissolved bodies which occur in small quantities in the serum. It thereby takes away the small quantities of immune-bodies, of alexins, or generally of antibodies contained in the antigenes, *i.e.*, immune sera.

Evidently this is a kind of diversion of alexin. Gay therefore raises the objection against the explanation of Neisser and Wechsberg concerning their experiments of the diversion of alexin by means of immune bodies (against bacilli). Gay is of the opinion that the injected culture of bacilli contains many albuminous substances, which after their injection caused the production of specific precipitins in the immune serum. Gay supposes that it was these precipitins which caused a precipitate with the fluids accompanying the bacteria in Neisser's and Wechsberg's experiments, and that this precipitate "absorbed" the added alexin, so that it is by no means proved that the disappearance of the alexin was due to the presence of great quantities of immune body binding the alexin. Gay was probably led to this criticism because the explanation given by Neisser and Wechsberg is in many details inconsistent with common laws of chemistry. If the bacteria, as in my corresponding experiments with red blood-corpuscles, had been freed from the accompanying albuminous substances by washing carefully, then the diversion of alexin by means of the immune body would have been proved (see above, IX.).

Gay has made similar experiments with red blood-corpuscles (0.05 cc.) from an ox, but he added half the quantity of ox-serum, freed from alexin by heating to 55°. With these he mixed a given quantity (0.033 cc.) of alexin (normal serum from rabbits), and varying quantities of serum from a rabbit, immunised with red blood-corpuscles from an ox. Then he added so much isotonic salt-solution that the total volume was 2.6 cc. He observed a very strong diversion of the alexin, so that the hemolysis was complete if the added quantity of immune serum was between 0.1 and 0.3 cc. With 1 cc. of immune serum the hemolysis was weak, and with 2 cc. or more it was imperceptible.

This method of determining the presence of a precipitate by means of its aptitude to absorb alexin is much more sensitive (about 100 to 1000 times) than the observation of the precipitate itself. It has therefore been used for discriminating the species of animal from which a given blood-spot is derived, instead of the older method of Wassermann and Uhlenhuth, in which the precipitate

itself was observed. The new method, which was worked out by Neisser and Sachs, plays a highly important rôle in the method of Wassermann for determining the presence of spirochaetes, or, better, their excretions, in human blood.

As will be seen from what has been said, immunochemistry has, during its short time of application, been able to explain the chief empirical facts of immunity, and there is good reason to hope that it will be able to throw light on the whole of that important branch of therapy and to transform it into a rational science.

Physical chemistry itself has thereby gained a great extension of its sphere, not only as regards chemical equilibria, but also as regards the study of velocities of action.

METHOD FOR NICKEL-ZINC SEPARATION IN GERMAN SILVER AND OTHER ALLOYS.

By LA VERNE W. SPRING.

THE nickel-zinc separation has always been a serious matter for the chemist who had to do it only occasionally and nearly as forbidding for him who was so unfortunate as to encounter it regularly. It was one of those things from which he was praying to be spared, but which he felt he could sometimes do little to avoid.

Some of the modifications of the sulphide separation can be made to work, but it is no method for a busy laboratory or for inexperienced hands. The fixed alkali hydroxide method is open to objections. The titration of the nickel with potassium cyanide in the presence of sodium pyrophosphate works at least approximately under the proper restrictions, but does not allow of a direct determination of the zinc.

Since the announcement during the past three or four years of the German methods for direct precipitation of nickel as nickel glyoxime or as nickel dicyandiamidine from solutions of almost any other metals, our own troubles have ceased quite completely. The analysis of German silver means now little more than analysis of a brass, and the new methods could be used advantageously by many more chemists than appear to be using them. I do not claim originality in the method as used in our laboratory for the past two years, for though I do not know that certain parts of the method have ever been published, they have, in a way, been forecast by the German chemists, Grossmann, Brunck, *et al.*, in articles in the German chemical magazines. The method is as follows:—

Weigh out one-half gm. of the drillings, or more, according to the percentage of the constituents; take out the tin with nitric acid, the lead as sulphate, copper by electrolysis, and iron with ammonia as usual. Add five grms. of ammonium chloride. Make the solution just neutral with hydrochloric acid, and add four-tenths of a gm. of dimethylglyoxime dissolved in a little alcohol for every tenth of a gm. of nickel supposed to be present. Add ammonia, drop by drop, until the solution smells slightly ammoniacal. Let stand just below the boiling point for one half-hour (more or less according as the nickel separates completely). Filter hot through counterpoised filters or on a weighed gooch, wash with hot water, and dry in the air-bath at 105° C. to constant weight. Weigh and calculate the nickel.



Until a little experience has been acquired, the filtrate should be tested to make sure that no nickel has escaped precipitation. Add 0.05 gm. more of the dimethylglyoxime in a little alcohol, see that the solution is just ammoniacal, and let stand for a few minutes. There should be no reddening of the solution, which would mean more nickel. Make the filtrate just acid with concentrated hydrochloric acid and add an excess of ten cubic centimetres. Boil for ten minutes to break up the dimethylglyoxime in the solution, add ten grms. of microcosmic

salt dissolved in a little water, neutralise with ammonia and hydrochloric or acetic acid until the solution neither turns blue litmus-paper red nor red paper blue, and let stand just below the boiling point (do not let bump) until the precipitate has become granular. Filter under suction, wash with hot water, ignite in a weighed porcelain crucible, cool, and weigh as zinc pyrophosphate, $\text{Zn}_2\text{P}_2\text{O}_7 \times 0.42913 = \text{Zn}$.

Dimethylglyoxime can be bought for 2.50 dols. per ounce.—*Journal of Industrial and Engineering Chemistry*, ii., No. 4.

NOTICES OF BOOKS.

The Phase Rule and its Applications. By ALEX. FINDLAY, M.A., Ph.D., D.Sc. Third Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911. (6s.).

IN the third edition of this monograph upon the Phase Rule and its Applications some paragraphs and sections have been added dealing with recent work, and a few verbal alterations have been made. A brief outline is given of the method of deducing the rule mathematically, the reader being referred to works on thermodynamics for fuller details. The application of the rule to the study of the formation of minerals is also discussed, and the important question of the metastability of metals is alluded to. Some additions have also been made to the chapter on isothermal solubility curves.

Triumphs and Wonders of Modern Chemistry. A Popular Treatise on Modern Chemistry and its Marvels. Written in Non-technical Language for General Readers and Students. By GEOFFREY MARTIN, B.Sc. (Lond.), M.Sc. (Bristol), Ph.D. (Rostock). London: Sampson, Low, Marston, and Co., Ltd. 1911.

THE author has taken the science of chemistry in its broadest possible aspect, and equipped with a sound knowledge of the subject in its latest developments, has set about to tell its marvels and wonders in a way that can scarcely fail to engage the interest of both old and young. In these times of multiplicity of books on chemistry written chiefly in view of the "examination" which looms like a nightmare before the student mind, it is a real pleasure to follow the author in his distinctly original exposition. Himself a teacher of considerable experience, the author's aim has been to present the fundamental principles of chemistry in such a way as to secure the interested attention of the reader. The style of the book reminds one of Prof. Pepper's "Play Book of Metals" of one's early days. Many of the chapters have been revised by leading authorities upon the subjects presented: thus we note the name of Sir William Crookes connected with Nitrogen and our Food Supply; Mr. Frederick Soddy, on Radio-active Elements; Dr. Caven; Mr. Golding, F.I.C.; Miss Ida Freund; W. C. D. Whetham; Sir William Ramsay; Mr. J. E. Gore, F.R.S.; Mr. Edwin Streeter; Rudyard Kipling, and others. The book contains some 350 pages, with 75 illustrations, mostly original, and is well printed and indexed; it is already becoming popular as a "gift book" for school prizes and like purposes.

Traité d'Analyse des Substances Minérales. ("Treatise on the Analyses of Mineral Substances"). By ADOLPHE CARNOT. Vol. III. Part I. Paris: H. Dunod and E. Pinat. 1910. (27 fr. 50).

THE third volume of this treatise is devoted to the analysis of the metals of the alkalis and alkaline earths, the rare earths, and the metals of the iron group. The properties of the chief compounds of each metal are discussed, and methods of determination, gravimetric, volumetric, and colorimetric, are described in full. The quantitative

analysis of the chief minerals is also treated. The author points out which processes are to be regarded as most satisfactory from the points of view of rapidity, accuracy, and simplicity, but in every case a large choice of methods is described, and the treatise is both comprehensive and detailed.

CORRESPONDENCE.

THE ATOMIC WEIGHT OF ACTINIUM.

To the Editor of the Chemical News.

SIR,—I am not aware that anyone has attempted to work out the atomic weight of actinium by an altogether satisfactory method of comparison with the other radio-active elements.

The following procedure, though not entirely new, may present a novel feature, in that the accompanying table is quite regular as regards the distribution of the α -, β -, and γ -rays, or particles. The atomic weights are also regular.

At. wts. of 1st elements.	Groups.	Rays.			Supposed end-products.	At. wts.
		α .	β .	γ .		
238.5	Uranium..	8	4	3	Lead ..	206.5
232.5	Thorium ..	6	3	2	Bismuth	208.5
226.5?	Actinium..	4	2	1	————	210.5

This arrangement lends support to the idea that three parallel lines of disintegration take place, in which the chemical properties run nearly parallel in many instances. See table by Cameron, *Nature*, 1909, lxxxii., p. 67).

It would appear, therefore, that the atomic weight of actinium was near to that of radium, and that the final stable product was an element analogous to tellurium, as predicted by Mendeleeff, and occupying the gap below bismuth.—I am, &c.,

F. S. LORING.

July 31st, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 22, May 29, 1911.

Oximes and Phenylalkylisoxazones obtained with Ethyl, Methyl, and Dimethylbenzoylacetic Ethers.—A. Haller and Ed. Bauer.—The compound described by Hantzsch and Miolati as the oxime of benzoyl ethylacetic acid is phenylethylisoxazoline. When the monomethyl, monoethyl, and dimethylbenzoylacetic ethers are treated with hydroxylamine and alcoholic potash they always yield substituted phenylisoxazolones. The same substituted ethers when subjected in alcoholic solution to the action of hydroxylamine chlorozincate yield oximes, which are saponified by potash, giving an alkaline salt from which an acid oxime is obtained on treatment with acid.

Radiations which Decompose Water.—A. Tian.—The rays which decompose water with formation of hydrogen peroxide occur in the extreme ultra-violet beyond about 1900 Angström units. The light of a mercury quartz lamp causes this decomposition, owing to the rays 1846, 1848, and 1851. A spark between aluminium electrodes possesses the same property.

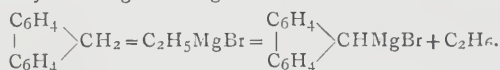
Catalytic Isomerisation of Acetylenic Pinacone.—Georges Dupont.—When acetylenic pinacone is subjected

to the action of mercuric sulphate it undergoes isomerisation, yielding tetramethylketohydrofuran, a mobile colourless liquid smelling of camphor. It readily gives a semicarbazone and a phenyl hydrazone. It behaves like a phenol in a series of reactions, and possesses both acid and basic properties.

New Method of obtaining β -Diketones.—Emile André.—The acetylenic ketones combine with the ethylenic amino-ketones in presence of hydrochloric acid and ferric chloride to give the ferric salts of the β -diketones. By this method the author has prepared the following β -diketones:—Acetylacetophenone, propionylacetophenone, butyrylacetophenone, isovalerylacetophenone, &c.

Tetrollic Aldehyde.—P. L. Viguier.—Tetrollic aceta can be obtained from crotonic aldehyde by Claisen's method. It is easily hydrolysed by dilute acids, and to obtain the pure aldehyde it is best to distil it with a 10 per cent solution of oxalic acid and extract the distillate with ether. Tetrollic aldehyde is a mobile liquid with an irritating odour; it readily oxidises in air, giving crystalline tetrollic acid. It reduces ammoniacal silver nitrate and Fehling's solution, and gives the normal bisulphite compound $C_4H_4O.SO_3.HNa$. With hydroxylamine and hydrazine it yields methylisoxazol and methylpyrazol.

Magnesium Derivative of Fluorene.—V. Grignard and Ch. Courtot.—The CH_2 group of fluorene is sufficiently acid to give a magnesium derivative:—



The authors have studied the reactions of the compound, and have prepared from it tertiary fluorenyl-fluorenol. The fluorenols are more stable than the corresponding diphenylated alcohols.

Bulletin de la Société Chimique de France.

Vol. ix.—x., No. 10, 1911.

Gases Evolved by Walls of Glass and Porcelain Tubes.—Marcel Guichard.—Gas is evolved by the walls of Jena glass tubes, slowly in the cold and more quickly on heating. Above 600° no further evolution takes place. With porcelain tubes the amount of gas is very variable, even with tubes of the same origin. Opaque silica tubes continue to yield large volumes of gas for some time.

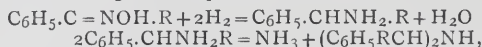
Preparation of Alkaline Metals.—Louis Hackspill.—The author describes a simple apparatus for preparing potassium by heating potassium chloride with excess of calcium. The yield is good, but the metal always contains some calcium and must be re-distilled.

Acyclic Keto-diacids.—E. E. Blaise and H. Gault.—The ethers of dibasic acids unite with oxalic ether in presence of sodium ethylate, giving the corresponding ketotriethers. These ethers, which have the ketone function in the β -position with regard to one of the carboxyls, when saponified lose one molecule of carbon dioxide and give rise to the α -keto-diacids. Thus α -keto-glutaric acid, $COOH.CO.CH_2.CH_2.COOH$, may be obtained. The authors have thoroughly investigated it and its derivatives.

Sparteïn.—Charles Moureu and Amand Valeur.—When the dichlorhydrate of α -methyl sparteïn is heated in a current of hydrochloric acid the dichlorhydrate of isosparteïn is formed. The free base is obtained by decomposing the dichlorhydrate with an alkali. Isosparteïn yields two distinct iodomethylates, which differ from one another in the arrangement in space, with regard to the same nitrogen atom, of the methyl residue and the iodine atom.

Catalytic Reduction of Cyclic Oximes.—A. Mailhe and M. Murat.—Aromatic oximes can be reduced at a low temperature by hydrogen in presence of divided nickel, giving primary and secondary amines, while some by-

products are also formed. The reduction of cyclohexanone oxime by divided nickel and hydrogen gives rise to the formation of cyclohexylamine and dicyclohexylamine. The catalytic reduction of cyclic ketoximes is not effected as easily as that of the aliphatic ketoximes. Besides the normal reactions leading to the formation of a small amount of primary amine and a larger quantity of secondary amine, according to the equation—



several secondary reactions occur, e.g., the original acetone is regenerated by the water vapour formed, and also the primary amine is decomposed into ammonia and ethylene hydrocarbon.

—

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 9, 1911.

Sulphur Phosphorus Compounds.—J. Mai.—When P_4S_3 is heated with sulphur in presence of petroleum a fused mass of P_4S_7 is obtained. P_4S_{10} is formed when P_4S_3 , sulphur, and naphthalene are heated together, and by using the theoretical proportions of the constituents P_4S_7 can be obtained similarly. P_4S_7 is converted into P_4S_{10} by heating to boiling with sulphur in naphthalene.

Alkyl Compounds of the Stannous Series.—P. Pfeiffer.—By reducing diethyl tin chloride in boiling ethereal solution in a current of hydrogen with sodium amalgam diethyl tin is formed. It is a yellowish liquid, which is soluble in benzene and ether. It is completely decomposed when heated. If the ethereal solution is allowed to stand it deposits a precipitate of diethyl tin oxide. It readily yields the diethyl tin halogens $(\text{C}_2\text{H}_5)_2\text{SnX}_2$. In composition and properties diethyl tin closely resembles the stannous halogen compounds SnX_2 . Diethyl tin can also be prepared by treating stannous chloride in an ethereal solution with ethyl magnesium bromide.

Compounds of Dysprosium.—G. Jantsch and A. Ohl.—Dysprosium bromate, $\text{Dy}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$, is formed from the sulphate by double decomposition with barium bromate. It crystallises in hexagonal crystals, which melt at 78° . It is soluble in water, and difficultly soluble in alcohol. Dysprosium selenate, $\text{Dy}_2(\text{SeO}_4)_3 \cdot 8\text{H}_2\text{O}$, can be obtained by the action of concentrated selenic acid on the nitrate. Dysprosium phosphate, $\text{DyPO}_4 \cdot 5\text{H}_2\text{O}$, separates as a crystalline precipitate when a solution of sodium phosphate containing ammonia is added drop by drop to a solution of dysprosium nitrate. It is white with a tinge of yellow, almost insoluble in water but soluble in dilute acids. The chromate, which crystallises with ten molecules of water and is a yellowish green crystalline powder, is obtained similarly. The carbonate, $\text{Dy}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$, is formed when carbon dioxide is passed over the hydroxide mixed with water. Dysprosium forms an ammonium double carbonate, $\text{Dy}(\text{CO}_3)_3\text{NH}_4 \cdot \text{H}_2\text{O}$, and a platinum cyanide, $[\text{Pt}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$, which crystallises in red crystals, turning white when heated. It is readily soluble in water, giving a yellow solution. The acetate and formate can be obtained by dissolving the hydroxide in the corresponding acid, and the oxalate by the addition of oxalic acid to a solution of the nitrate.

Chemical Light Actions.—Giacomo Ciamician and P. Silber.—Under the action of light a mixture of acetone and methyl alcohol gives isobutylene glycol and some isopropyl alcohol as well as ethylene glycol. Acetone and ethyl alcohol give trimethyl ethylene glycol, isopropyl alcohol, and other substances which have not been identified. Acetone and isopropyl alcohol yield only pinacone.

Use of Ether in Metallic Analysis.—F. Mylius and C. Hüttner.—The authors have determined exactly the amounts of chloride extracted by ether from mixtures of

metallic chlorides. They find that the presence of free hydrochloric acid has no effect upon the extraction. The ether method is very useful in gold analysis.

MISCELLANEOUS.

Institute of Chemistry.—Pass List, June-July Examinations, 1911.—Examinations were held in London and Glasgow.—Of thirty-one candidates who presented themselves for the Intermediate Examination the following seventeen passed:—J. L. S. Allan; K. C. G. Arbutnot, B.A.; R. Clark; T. W. Derrington; E. C. Evans, B.Sc.; H. Gilmour; R. E. Griffiths, B.Sc.; C. L. Hinton; R. P. Keith; J. G. King; R. Linch; B. B. Murdoch, M.A., B.Sc.; M. J. Robb, B.Sc.; J. W. Tait, M.A.; F. G. Tarn; T. A. Wilson; F. G. C. Walker. Of thirty-four candidates who presented themselves for the Final Examination for the Associateship, twenty-three passed. In the Branch of Mineral Chemistry—G. Hamilton; S. R. Illingworth, A.R.C.S.; E. A. Masters, B.Sc.; C. B. Roos, B.Sc.; J. Sorley; A. F. Suggett. In the Branch of Physical Chemistry—Arthur Bramley, B.Sc., A.R.C.S. In the Branch of Organic Chemistry—E. Anderson; O. L. Brady, B.A.; D. S. Dawson, B.Sc.; W. Jewell; J. A. McRae, M.A.; W. G. Prescott; S. P. Schotz; D. B. Steinberg, B.Sc.; J. C. White; L. Wilson, B.Sc. In the Branch of the Chemistry of Food and Drugs, Fertiliser and Feeding Stuffs, Soils and Water—H. J. Evans; Miss M. Gazdar, B.Sc.; H. Lowe, B.Sc.; W. R. Pratt; H. B. Stevens; J. A. L. Sutcliffe. Of four candidates examined for the Fellowship, two passed in the Chemistry of Food and Drugs, &c.—J. Hawthorne, B.A., Ph.D., and A. Miller, M.B., M.R.C.S., Major I.M.S.; and one a Special Examination in General Chemistry—G. H. Stanley, A.R.S.M. One candidate for the Intermediate Examination presented himself at Singapore in June, and passed—A. M. Bailey. The Board of Examiners reported on seventy candidates in all, and of these forty-four passed.

City and Guilds of London Institute.—On the report of the Delegacy charged with the management of the City and Guilds (Engineering) College the Council of the City and Guilds of London Institute on July 24th awarded the diploma of "Associate of the City and Guilds of London Institute" to the following matriculated third year students of the City and Guilds College who have completed a full course of instruction as prescribed by the Council:—**Diplomas.**—Civil and Mechanical Engineering (56)—C. O. C. Reilly (Bramwell Medal), E. C. Abbott-Young, H. W. Ash, W. B. Ayres, H. W. Beale, F. R. Blackmore, G. L. H. Bradley, R. C. Brown, J. S. Burns, A. P. Cole, T. Dass-Kochhar, F. W. Davey, J. W. L. Davies, C. A. A. Elliot, A. L. Evans, S. E. Faber, A. G. T. Glaisby, J. L. Grant, C. F. Highett, H. B. R. James, A. R. C. Jenks, C. R. H. Kane, R. A. Knight, V. K. Kunte, L. Lacey, B. M. Lal, A. B. Lawson, H. L. Leicester, W. J. Lodge, J. H. Mair, G. J. Malcolm, T. H. J. Maringe, H. Mawson, A. C. McHatton, J. A. Miles, J. C. Mills, F. E. Mocatta, A. V. Nicolle, G. Osmand, R. F. Parkinson, C. L. Patrick, N. D. Quirk, D. Reeves-Smith, H. A. Reid, J. M. de las Rivas, C. G. Ruck, J. G. Schon, A. C. Smith, N. J. Sossidi, J. A. Stein, R. V. W. Stock, B. L. Subarwal, J. A. Tennant, A. J. White, H. D. Wilkinson, H. G. Wilkinson. **Electrical Engineering (30)**—A. H. Barrett (Siemens Memorial Medal), W. B. Bacon, W. E. Barker, A. S. M. Best, M. de Castro, S. N. Chopra, C. A. Claremont, H. J. Eley, E. P. Elworthy, C. F. Freeborn, C. L. Hall, N. P. Hinton, T. J. Hornblower, A. N. Kingsbury, W. H. Lovell, A. A. Maytham, B. McCormick, T. E. de Morsier, W. W. P. Page, E. Potter, S. M. Rawson, A. Riddle, H. W. D. Rock, P. G. Rider, C. W. Saunders, G. F. R. Schmidt, G. J. Scott, R. W. Shackell, W. Still, C. Vandermin. **Chemistry Department (10)**—G. G. Carter, B. G. Donne, H. W. Gosney, R. S. Haskew, J. F. Potts, L. W. Quelch, W. H. Robertson, N. E. Siderfin, E. E. Walker, D. S. Zossenheim.

THE CHEMICAL NEWS.

VOL. CIV., No. 2698.

A NEW METHOD FOR THE SEPARATION OF CERIUM.

By C. JAMES and L. A. PRATT.

CERIUM differs from the other elements of the rare earths in that it forms a series of more highly oxidised compounds. It is a well-known fact that many of these ceric compounds very readily undergo hydrolysis, and this property has been made use of for the separation of the element. Cerium, material obtained by those methods which give a precipitate of hydrated ceric oxide, is usually less pure than that obtained from operations giving basic salts. Hitherto the great disadvantage of precipitating cerium as basic ceric nitrate has been, that only a portion of the cerium could be thrown out of solution. The authors found that potassium bromate is capable of oxidising cerous nitrate in a faintly acid or neutral solution, so that this element may be entirely separated from the other rare earths.

When a solution of the rare earth nitrates is boiled with potassium bromate in the presence of a lump of marble (Saccharoid limestone), the cerium is entirely precipitated as the basic ceric nitrate, with varying amounts of basic ceric bromate. The cerium obtained in this manner is free from other rare earths, if the operation has been carefully conducted.

In working on a large scale with concentrated solutions, it is advisable to use a slight excess of bromate, and to stop the action while a little (about 1 per cent) cerium remains in the liquid. Under these conditions a cerium product is obtained, which, after washing with a 5 per cent ammonium nitrate solution, gives a pale straw coloured oxide. A saturated solution of the nitrate of this material shows no trace of absorption spectrum when tested with a layer 20 cm. thick.

Experimental Data.

A solution of pure cerium nitrate was prepared and standardised by precipitating with oxalic acid, and igniting to CeO_2 . Ten cc. contained 0.4068 gm. CeO_2 .

In a similar manner a solution of didymium nitrate was made and standardised.

Ten cc. contained 0.4109 gm. of the oxide.

Many experiments were performed in the endeavour to find an ideal substance with which to keep the liquid neutral. The results obtained are given below.

(a) *Lump Marble*.—Ten cc. of each of the standardised solutions, together with 5 grms. of potassium bromate, were diluted to 100 cc., a piece of marble added, and the whole boiled. After a few minutes, a yellow precipitate began to form, and free bromine was evolved. The precipitate was filtered, washed with a 5 per cent solution of ammonium nitrate, and dissolved in hydrochloric acid.

It was found necessary to dissolve the precipitate in the beaker previously used, owing to the fact that it was impossible to wash all ceric basic nitrate from the sides of the vessel. The hydrochloric acid solution was boiled, cooled, and filtered. The clear filtrate was evaporated to remove the excess of acid, then diluted, and the cerium precipitated as the oxalate. Six experiments carried out in this manner, the time of boiling being varied, gave the results shown in the accompanying table.

Ten cc. of the didymium solution free from cerium were boiled with potassium bromate and marble for thirty minutes, and in this case no precipitate formed.

No.	Time (mins.)	Wt. of CeO_2 (found).	Wt. of CeO_2 (theoretical).
1.	15	0.3896	0.4068
2.	20	0.4083	"
3.	25	0.4076	"
4.	30	0.4102	"
5.	35	0.4123	"
6.	45	0.4144	"

(b) Powdered marble, lead carbonate, zinc carbonate, zinc oxide, copper carbonate, and copper oxide caused the solution to become rapidly alkaline, which hindered the oxidation by the bromate.

(c) *Magnesite* proved to be much slower in its action, and owing to the fact that the mineral lacked uniformity in contour the basic ceric salts entered the crevices and could not be washed out.

(d) *Dolomite* would undoubtedly serve the purpose of ordinary marble if sufficiently pure. The specimens available for our experiments contained iron, and were unsuited for the work.

The important fact, brought out by the above experiments, and others not included, is that lump marble, presenting as it does comparatively small surface, is the best material with which to keep the solution in a proper state of acidity for the oxidising action of the potassium bromate. It should be specially noted that powdered marble is not applicable, as the neutralisation is carried so far that the product is contaminated with didymium.

Quantitative Estimation.

Since no satisfactory gravimetric method for the estimation of cerium is known, the authors considered it worth while to attempt to apply this process for quantitative work. In this endeavour a double precipitation was carried out, using a smooth lump of marble (containing no crevices), so that any adhering precipitate could be easily washed therefrom. The first precipitation was continued until the mother-liquor failed to give a test for cerium. This point was determined by withdrawing a small quantity of the supernatant liquid with a pipette, and applying the hydrogen peroxide test. When the liquid was found to be free from cerium, the precipitate was filtered and washed with a 5 per cent solution of ammonium nitrate. The filter-paper with the precipitate was returned to the beaker, and treated with nitric acid and a little potassium bromate to oxidise the paper. (It was found absolutely necessary to oxidise all the filter-paper, otherwise the cerium could not be precipitated, even after several hours' boiling). After having boiled the solution to remove the excess of acid, the residue was dissolved in water, and treated as before with potassium bromate and marble. The boiling was continued until the supernatant liquid failed to give a test for cerium. The precipitate was separated on a filter, washed with ammonium nitrate solution, placed in the original beaker, and dissolved in hydrochloric acid. The liquid was then filtered, evaporated to remove the excess of acid, the residue taken up with water, and the cerium precipitated as the oxalate. This was ignited, and the cerium weighed as CeO_2 . The following results were obtained:—

	CeO_2 (found).	CeO_2 (theoretical).
1. . . .	0.4100	0.4068
2. . . .	0.4094	0.4068

The Purification of Cerium on a Large Scale.

The material used for this work consisted of the monazite earths freed from thorium. The oxides were dissolved in nitric acid, the concentrated solution made nearly neutral, heated to boiling, and potassium bromate added. As soon as red fumes of bromine made their appearance two or three large pieces of marble were placed in the container, and the boiling continued for a few hours. The length of the operation depended upon the amount of cerium in the solution. Small portions were withdrawn at intervals, and

as soon as it was ascertained, by the hydrogen peroxide test that nearly all the cerium had been thrown out of solution, the boiling was discontinued. The marble was then removed, and the precipitate allowed to settle. The clear supernatant liquid was syphoned off, and the precipitate washed upon a Buchner funnel with a 5 per cent solution of ammonium nitrate. The basic salt was dissolved in hydrochloric acid, and the filtered solution treated with oxalic acid. Sometimes, however, it was found more advantageous to precipitate the cerium as the sulphate by gradually adding concentrated sulphuric acid to the chloride solution, and partially evaporating on the water-bath. Alcohol was added to the residue, the sulphate separated by filtration and washed with alcohol. For a final purification, the sulphate was rendered anhydrous, made into a saturated solution in cold water, and once again precipitated by heating.

The small amount of cerium remaining with the other earths in the original mother-liquor was next precipitated by boiling with potassium bromate and marble until some of the clear liquid no longer gave the hydrogen peroxide tests. This precipitate of cerium carrying a little of the other rare earths was dissolved in nitric acid, and added to the next batch for preparation of pure cerium.

The precipitate thrown down by this process varies very considerably, depending upon the conditions of the experiment. It was found, when concentrated solutions were used, that very dense precipitates were obtained. This is a very important point, since the light precipitates, obtained from dilute solutions, filtered with great difficulty. It was impossible to wash even the densest precipitates with water, owing to the formation of colloidal solutions. This difficulty was overcome by washing with a 5 per cent ammonium nitrate solution.

When a large excess of bromate was employed, the cerium was obtained chiefly as a basic ceric bromate. Under the best conditions, using only a slight excess of bromate, a basic ceric nitrate was obtained. On dissolving this precipitate in acid only a slight amount of bromine was evolved.

With too small amount of bromate, the solution became alkaline, the precipitate darkened in colour, and was found to contain didymium, &c. Such a precipitate was purified by dissolving in concentrated nitric acid with the help of a very little alcohol. The resulting solution, possessing a deep orange-red colour, gave a heavy precipitate upon diluting and boiling with marble. Care must be taken not to allow the solution to become alkaline by boiling too long.

By the bromate method, the authors obtained many kilograms of cerium salts of such a purity that a saturated solution of the nitrate gave no absorption bands when observed through a layer 20 cm. thick.

With a little experience the method is easily controlled, and the production of large amounts of pure cerium compounds is only a matter of hours.

It would seem that this method might well become commercially valuable, as potassium bromate can now be obtained quite cheaply.

Once again the authors desire to express their thanks to the Welsbach Company for material, through the courtesy of Dr. H. S. Miner.

Durham, N.H., Jan. 10, 1911.

Direct Preparation of Compounds of Sulphonic Derivatives with Mineral and Organic Bases.—A. Seyewetz and L. Poizat.—Many sulphonic derivatives can be precipitated as the sodium salt by adding the theoretical amount of sodium chloride to the raw product of sulphonation. This method the authors have successfully applied to the preparation of salts of monobenzene sulphonic acid, not only with mineral bases, but also with the organic bases, amines, hydrazines, hydroxylamine, urea, aminophenol.—*Bull. Soc. Chim. de France*, ix., No. 6.

RECENT ADVANCES IN HIGH-TEMPERATURE GAS THERMOMETRY.*

By ARTHUR L. DAY, Ph.D.

Director of the Geophysical Laboratory of the Carnegie Institute of Washington.

(Concluded from p. 53).

3. *The Furnace.*—Improvements in the furnace have twice contributed materially to the advancement of gas thermometry. (1) Through the substitution of electricity for gas as a source of heat (Reichsanstalt, 1899), which greatly reduced the uncertainty in temperature distribution over the bulb surface and eliminated the possibility of furnace gases passing into the thermometer itself through the bulb wall; and (2) when the bulb and heating coils were enclosed in an air-tight bomb (Geophysical Laboratory, 1908) under conditions such that the gas pressure outside of the bulb could be kept under control and always maintained equal to the pressure of the expanding gas within.

This second improvement made it possible (1) to maintain a nitrogen atmosphere with equal pressure both inside and outside of the bulb and thus to obviate any tendency of the gas to diffuse through its wall; (2) to relieve the bulb from mechanical strain at high temperatures where the metal is soft and susceptible to volume changes, which considerably increases the effective range of the instrument in the high-temperature region; and (3) to increase the sensitiveness of the instrument more than threefold. It also became possible to use different initial pressures within the thermometer bulb in order to evaluate the pressure coefficient of the expanding gas and to vary the sensitiveness of the instrument.

Before this improvement was made it was necessary to select an initial gas pressure such that the final pressure at the highest temperature to which it was expected to attain would be approximately equal to the atmospheric pressure without, in order that the difference in pressure within and without the bulb should be a minimum when its power to withstand such a difference was smallest. The practical effect of the earlier arrangement was to crowd the entire range of the instrument into 500 mm. of the manometer scale, giving about $\frac{1}{3}$ mm. per degree. With the air-tight furnace bomb we were able to increase this sensitiveness to a full millimetre for each degree.

To the introduction of electric heating we owe the extension of the range of the gas thermometer from 1150° to 1500°; to the control of the gas pressure about the bulb, a considerable (perhaps five-fold) increase in its accuracy in this region.

With electric heating the furnace temperature is always under control and readily measurable, but in pursuing high standards of accuracy we must distinguish between a constant furnace temperature of irregular distribution and a variable temperature. The substitution of electricity for gas has given us a constant temperature, but it is not always easy to provide that it shall also be perfectly uniform everywhere about the bulb.

Various baths are available up to perhaps 700° for the purpose of equalising the temperature about the bulb by interposing between it and the heating coil a liquid layer which can be stirred, but higher temperatures have had to depend upon direct exposure to the radiation from the coil. In the Reichsanstalt instrument temperature differences of from 10° to 30° were observed between the middle and ends of the bulb in the region 1500° to 1600°; in that of the Geophysical Laboratory, the maximum differences were diminished to 2° in the same region.

For greater uniformity than this some form of liquid bath will require to be devised for use at these temperatures also. Such a search might prove worth while, for his uncertainty (in the distribution of temperature about the bulb) appears to be the largest remaining in gas thermometry up to 1550°.

* A paper read before the Faraday Society, May 23, 1911.

Substance.	Point.	Atmosphere.	Crucible.	Temperature.	The Reichsan stalt scale.
Zinc. . . .	Melting and freezing	Air	Graphite	$418.2^{\circ} \pm 0.3$	419.0°
Antimony . .	Do.	Carbon monoxide	Do.	629.2 ± 0.5	630.6
Silver. . . .	Do.	Do.	Do.	960.0 ± 0.7	961.5
Gold	Do.	Do.	Do.	1062.4 ± 0.8	1064.0
Copper	Do.	Do.	Do.	1082.6 ± 0.8	1084.1
Diopside (pure)	Melting	Air	Platinum	1391.2 ± 1.5	
Nickel	Melting and freezing	Hydrogen and nitrogen	Magnesia and magnesium aluminate	1452.3 ± 2.0	
Cobalt	Do.	Do.	Magnesia	1489.8 ± 2.0	
Palladium. . .	Do.	Air	Pure magnesia	1549.2 ± 2.0	1575
Anorthite (pure)	Melting	Do.	Platinum	1549.5 ± 2.0	

In addition, the following temperatures were incidentally obtained :—

Cadmium . . .	Melting and freezing	Air	Graphite	320.0 ± 0.3	321.7
Aluminium . .	Freezing	Carbon monoxide	Do.	658.0 ± 0.6	657
Platinum . . .	Melting	Air		$1755 (a) \}$ $1752 (b) \}$	± 5

(a) Extrapolation optical.

(b) Extrapolation thermo-electric.

4. *The Manometer.*—The manometer contains few factors which affect the ultimate temperature readings materially. The arrangement commonly adopted, both in Europe and in the United States, is the open U-tube type, in which the difference in the mercury level between the two arms of the U-tube represents the difference between the gas pressure within the bulb and the prevailing atmospheric pressure outside, the latter being read on a separate barometer. The minor corrections for temperature of the mercury, gravity, &c., then require to be applied as usual in such cases.

The only real difficulty encountered here has been much reduced in recent years and is no longer dangerous, even at the highest temperatures. The temperature of the capillary connection between the bulb and manometer varies all the way from the extreme temperature of the bulb to that of the room and with it the temperature of so much of the gas as it contains. The error from this cause is reduced to an insignificant magnitude by making this connecting volume so small when compared with that of the bulb that its average temperature need only be known within about 10 per cent.

Some laboratory experience is necessary to make this reduction of volume judiciously, for the viscosity of gases increases rapidly with the temperature, so that it is not practicable to restrict below 0.8 mm. the diameter of those portions of the capillary which are heated. A smaller diameter here would have the effect of producing a very slow readjustment of pressure in the various parts of the apparatus with every change in the temperature, and the observer would be without adequate assurance that equilibrium had been reached at the time when his reading was made.

The uncertainty which attaches to this connecting volume, together with the changes in the zero-point due to the irregular behaviour of porcelain bulbs, were among the most formidable of the classic errors of gas thermometry. Both are now practically eliminated.

5. *The Auxiliary Thermoelement.*—The fact that the gas-thermometer bulb cannot be safely immersed in different substances for the determination of their thermal constants carries with it a considerable amount of incidental but practically unavoidable inconvenience. The usual plan has been (and still is) to place thermoelements in the furnace with the bulb and to determine their electromotive force for a measured temperature. A few observations of this kind suffice to establish an empirical curve for the electromotive force of the thermoelement in terms of the gas thermometer temperatures, after which the thermo-

element is available for determinations of temperature under a great variety of conditions.

This procedure is considerably facilitated by the fact that the empirical curve corresponds closely to a simple parabola, and three or four comparisons with the gas thermometer usually suffice to establish a parabolic curve which may be interpolated with little danger of an error greater than the errors of the gas scale itself over long ranges of temperature. Its extrapolation has not turned out so fortunately.

Before the publication of the recent measurements made in the Geophysical Laboratory, the region of accurate gas thermometry ended with the temperature 1150° . The common practice for some years has therefore been to measure temperatures beyond that point by extrapolating this parabolic curve of electromotive forces out to the desired temperature—often as high as the melting-point of platinum (1755°). Extended extrapolation is always a matter of grave uncertainty, but no other convenient method was available, and, after all, observations of this kind with the thermoelement could be translated in terms of an observed scale whenever one should be provided. It happens in this particular case that the extrapolation (from 1150° to 1755°) comes out just 50° low at the platinum melting-point.

Now that the gas thermometer is able to make direct measurements of temperature up to 1550° it is merely necessary to include several thermoelements in the furnace with it, to evaluate their temperature curves by direct comparison, and afterward to determine with them a series of standard fixed temperatures like the melting-points of metals, minerals, or salts, which are available for general use.

This procedure has been followed in the recent investigation at the Geophysical Laboratory, with the results which are tabulated in the accompanying table. The pure metals are readily obtainable and the minerals easily made up, so that any one may now calibrate his thermoelement by noting its electromotive force at the (known) melting temperature of three or four of these substances, preferably choosing such as will include the region in which he expects to use the thermoelement.

Such a calibration requires to be checked from time to time by repeating one or more of the melting-point observations, particularly if the element is exposed to contamination from vapours of other metals. This contamination is particularly disastrous if a thermoelement is exposed to the vapour of iridium, which explains the remark made above, that in our experience a bulb made from an alloy

of platinum and rhodium is to be preferred to the iridium alloy in use at the Reichsanstalt.

The standard melting-points in the table are taken from observations by Day and Sosman (*loc. cit.*, p. 161), and include, for comparison, the standard melting-points published by the Reichsanstalt in 1900, and now in general use.

A new estimate of the melting-point of platinum, which has not yet been directly determined with the gas thermometer, is included in the above list. It was obtained in this way:—There is a remarkably close agreement between independent determinations by radiation methods of the temperature interval between the melting-points of palladium and platinum:—

Nernst and von Wartenberg (a)	204°
Holborn and Valentiner (at the Reichsanstalt) (b) . .	207
Waidner and Burgess (at the Bureau of Standards) (c) .	207
Mean	206

(a) W. Nernst and H. von Wartenberg, *Ber.*, 1906, iv., 48, 146).

(b) L. Holborn and S. Valentiner, *Ann. Phys.*, 1907, [4], xxii., 1.

(c) C. W. Waidner and G. K. Burgess, *Bull. Bur. Standards*, 1907, iii., 163.

If we, therefore, simply add 206° to the palladium melting temperature (1549°), we obtain 1755° as the melting-point of pure platinum, with an absolute error of perhaps no more than $\pm 5^\circ$.

Similarly, if we extrapolate the curve of thermal e.m.f. from the palladium point upward until the platinum wire of the thermoelement melts, we obtain a second estimate of the platinum melting-point. This has been carried out in the Geophysical Laboratory with several elements of standard composition (90 parts platinum, 10 parts rhodium) as well as with others (1, 5, and 20 per cent rhodium), giving a mean value of 1752°, in excellent agreement with the first extrapolation.

In conclusion, it may be pointed out that the thermoelement has now become a subsidiary instrument; of immense value as such because of its great convenience and sensibility, but untrustworthy when unsupported by adequate standards of reference because of its extreme sensitiveness to the contaminating influence of metal vapours.

The way is now open for a direct and accurate calibration of radiation pyrometers throughout the region between 900° and 1550°, which should afford a much more certain basis for extrapolation to those extreme temperatures which no laboratory apparatus can withstand.

A REVISION OF THE ATOMIC WEIGHT OF IRON.*

THIRD PAPER.—THE ANALYSIS OF FERROUS BROMIDE.

By GREGORY PAUL BAXTER,
THORBERGUR THORVALDSON, and VICTOR COBB.

1. Introduction.

The atomic weight of iron has already been subjected to two investigations in the Chemical Laboratory of Harvard College. In one ferric oxide was analysed by reduction (Richards and Baxter, *Proc. Amer. Acad.*, 1900, xxxv., 253), in the other the per cent of bromine in ferrous bromide was determined (Baxter, *Proc. Amer. Acad.*, 1903, xxxix., 245). The first investigation yielded as a result 55.883 (O = 16.000), a value somewhat lower than the one in general use at the time, 56.0. The result of the second investigation, 55.871 (Ag = 107.93)

confirmed so closely the value resulting from the oxide analysis, that, since the methods of the two investigations differ so radically, the matter was allowed to rest at this point until very recently. During the last few years much evidence has been brought forward to show that the older value for the atomic weight of silver, 107.93, is several hundredths of a unit too high, and that the probable value lies at least as low as 107.84. With this lower value for silver and a correspondingly lower value for bromine the atomic weight of iron calculated from the bromide analyses is 55.845. The agreement of this corrected value with the result of the analysis of the oxide is far from satisfactory. It becomes imperative therefore to discover, if possible, the cause of the difficulty and to determine which of the early results is more reliable.

Neither of the methods mentioned above is entirely free from difficulties. In the oxide method, either the presence of magnetic oxide in the ferric oxide or incomplete reduction would have caused too high a result to be obtained. Since in the experiments by Richards and Baxter, the oxide was made from the nitrate by ignition in air, it is not easy to believe that an error from the first cause actually exists. On the other hand, very prolonged ignition at a high temperature in a current of hydrogen is necessary to insure even apparently complete reduction of ferric oxide to metal. Two indications of complete reduction were obtained by Richards and Baxter, one of which was constancy in the weight of the metal when repeatedly ignited in hydrogen, the other of which was complete solubility of the metal in dilute acid. Either of these tests might be misleading, however, since oxide might be so coated over with metal as to prevent or delay further reaction with the hydrogen, while it is well known that the solubility of ferric oxide in acid is increased by the presence of ferrous salts. It is true that gases occluded by the ferric oxide and released during reduction might have caused too great a loss in weight and hence have lowered the observed atomic weight of iron. But careful tests were made for occluded gases and no appreciable quantity was detected.

While the analysis of halogen salts for halogen has been found to be one of the most satisfactory methods of atomic weight determination, the analysis of ferrous bromide, as carried out by Baxter, was subject to a slight uncertainty. The bromide was made by sublimation in porcelain tubes and contained between one- and two-tenths of one per cent of sodium bromide extracted from the tubes. The proportion of sodium bromide was unfortunately not as constant as could be desired, hence the correction which was applied for this impurity may be slightly in error.

On the whole, however, the ferrous bromide analysis seemed more satisfactory, and, since fused-quartz apparatus, which was not available for the earlier investigation, presented the possibility of many improvements in the preparation and analysis of the salt, it was decided, in taking up the subject anew, first to repeat the analysis of ferrous bromide.

2. Purification of Materials.

Water.—The ordinary distilled water of the laboratory was used in the preliminary stages of the purification of some of the materials used in this research, but for most purposes the laboratory supply was twice re-distilled, first from alkaline permanganate, and then from very dilute sulphuric acid. Condensers of block tin were employed and rubber or cork connections were entirely avoided. In general, the water was collected in Jena glass flasks, but for special purposes either platinum or quartz receivers were used.

Nitric Acid.—Commercial chemically pure nitric acid was purified by two distillations through a quartz condenser with the rejection of the first third of the distillate in each distillation. Nitric acid distilled in this way does not contain more than the merest trace of chlorine, if the original acid is fairly pure. Here also quartz or platinum receivers were used whenever traces of alkalis were to be avoided.

* From the *Journal of the American Chemical Society*, xxxiii., No. 3.

Sulphuric Acid.—The best commercial article was distilled from a non-tabulated glass retort into an air-cooled flask. The first portion of the distillate was rejected. This acid was never used where a trace of alkali would have been harmful.

Ammonia.—Pure commercial ammonia of sp. gr. 0.90 was heated in a glass-stoppered boiling flask and the gas was absorbed in the purest water.

Solid reagents.—Potassium permanganate, potassium dichromate, potassium and ammonium oxalates, and oxalic acid were purified by several crystallisations from aqueous solution, with centrifugal drainage.

Silver.—The sample of silver used in this investigation was purified by methods which have been thoroughly tested in this laboratory (see especially Richards and Wells, *Pub. Car. Inst.*, 1905, xxviii., 16; *Journ. Am. Chem. Soc.*, xxvii., 472). Silver chloride was precipitated from strongly acid solution and, after thorough washing by decantation, was reduced by means of sugar and sodium hydroxide. The metal was washed and fused upon charcoal before a blowpipe, and the surface impurities were removed from the buttons by scrubbing with sea sand and etching with dilute nitric acid. The cleansed buttons were dissolved in nitric acid, and the solution, after neutralisation, was precipitated with ammonium formate which had been prepared with distilled materials. Again the metal was thoroughly washed with water and fused with even more care than before in a porcelain crucible lined with the purest lime. The resulting buttons were in turn cleansed by etching with dilute nitric acid and were next converted into electrolytic crystals in a cell in which a concentrated, nearly neutral solution of silver nitrate served as electrolyte, and a pile of the buttons served as anode, the cathode being a stick of very pure silver from another preparation. After the crystals had been thoroughly washed with water, they were fused in a current of hydrogen in a porcelain boat lined with the purest lime. The boat was provided with cavities so that the buttons of silver varied considerably in size, from 2 to 5 grms. The final product was freed from adhering lime by etching with dilute nitric acid and, after being washed with the purest water, it was dried, first in air at 100°, finally in a vacuum at about 500°.

A second sample was prepared in an exactly similar fashion by Dr. H. C. Chapin (*Proc. Am. Acad.*, 1910, xlvii., 213; *Journ. Am. Chem. Soc.*, 1911, xxxiii., 16), for work upon the atomic weight of neodymium, except that it was necessary to cut the product into smaller fragments by means of a fine jeweller's saw. Surface contamination with iron from the saw was removed by etching with successive portions of dilute nitric acid until the acid remained free from iron. This specimen was used only in Analysis 13 and 27. Both specimens have already been used in a determination of the atomic weights of iodine and silver, and have been found to give results identical with those of other very pure specimens of silver (Baxter, *Journ. Am. Chem. Soc.*, 1910, xxxii., 1591).

Hydrobromic Acid.—This substance was prepared from bromine which had been carefully freed from chlorine and iodine by processes which have repeatedly been shown to be effective for the purpose in this laboratory. Commercial bromine was first distilled from solution in saturated aqueous potassium bromide. A portion of the product was next converted into potassium bromide by addition to a solution of twice re-crystallised potassium oxalate, and the remainder of the bromine was distilled from solution in this potassium bromide, which must have been at any rate nearly free from chloride. Although in these two distillations from a bromide the bromine must have been very effectually freed from chlorine, still another similar distillation was carried out later. The next step consisted in converting the bromine to hydrobromic acid. Hydrogen, made by the action of water on "hydrone," was purified and dried by scrubbing with water and passing over fused potassium hydroxide. This hydrogen was charged with a very nearly equivalent amount of bromine by bubbling through the latter substance at about 45°, and the mixture was passed

over hot platinised asbestos in a hard glass tube. The resulting hydrobromic acid was absorbed in the purest water. Needless to say, no cork or rubber connections were used in the apparatus for synthesising hydrobromic acid except to connect the hydrogen generator to the purifying apparatus. In order to free the hydrobromic acid from iodine the solution was twice boiled for some time, after the addition of a small amount of the specimen of bromine which was used in the preparation of the acid, and finally with a small quantity of chlorine-free potassium permanganate. The hydrobromic acid solution was next distilled and then was converted into bromine by heating with a nearly equivalent amount of chlorine-free permanganate. In this way, since only five-eighths of the bromine is set free, the product received a third distillation from a bromide. The bromine was again converted into hydrobromic acid in the way already described, and the acid solution was freed from excess of free halogen by boiling and finally by distillation. Three different specimens of hydrobromic acid prepared in the same way all gave identical results as far as could be determined.

Fuming hydrobromic acid was made by saturating the constant-boiling solution at 0° with hydrobromic acid gas synthesised as above. Especial care was taken to avoid an excess of bromine in the synthesising apparatus.

Iron.—The preparation of pure iron has been discussed in the earlier papers upon the atomic weight of iron. Essentially the same methods were used in the purification of the three specimens employed in this investigation.

Sample A was made from very pure iron ribbon. After solution in re-distilled nitric acid the ferric nitrate was three times crystallised from concentrated nitric acid with centrifugal drainage after each crystallisation. All the operations, even the centrifuging, were performed in platinum vessels.

The nitrate was next dried and partially decomposed by heating on an electric stove in a platinum dish. The resulting mixture of oxide and basic nitrate was reduced to metal by means of ammonia, generated from a concentrated solution by means of solid sodium hydroxide, and dried by the same substance. During the reduction, the oxide was contained in porcelain boats which were placed in a hard glass tube. Fused or ground connections were employed in the apparatus throughout. This sample of metal was used only for preliminary preparations.

Very pure metallic iron prepared by the American Rolling Mills Co. served as the starting-point in the preparation of Sample B. It contained sulphur 0.019 per cent, phosphorus 0.003 per cent, carbon 0.018 per cent, silicon, trace, manganese, trace, copper 0.05 per cent.

In the purification of this material exactly the same course was followed as in the case of Sample A, except that the nitrate was crystallised five times from concentrated nitric acid, and the oxide was reduced in hydrogen, generated electrolytically from a solution of potassium hydroxide, and dried by solid potassium hydroxide.

The purification of Sample C was even more thorough. The specimen of metal from the American Rolling Mills Co. was used here also. The block of iron, which was sawed from a larger piece, was washed first with ether, next with alcohol, and finally with water. A superficial layer was then removed by etching with dilute nitric acid, and the block was again washed with water. Upon dissolving the metal in re-distilled hydrochloric acid a small amount of insoluble matter remained, chiefly carbon in all probability. Without filtering, the solution was diluted with water and treated with hydrogen sulphide for some time, and a slight precipitate, consisting chiefly of sulphur and copper sulphide, was removed by filtration. On treating the solution twice more with hydrogen sulphide, only sulphur was precipitated. In this way all but traces of metals whose sulphides are insoluble in acids must have been eliminated.

In order to free the iron in particular from cobalt and nickel, it was next precipitated as ferric hydroxide by means of ammonia. First the ferrous chloride solution

was oxidised by boiling for some time with a considerable amount of nitric acid, and after dilution it was poured, with continual agitation, into a hot solution of re-crystallised ammonium nitrate containing a very large excess of re-distilled ammonia. The precipitate was then washed many times by decantation. The process was next repeated, after dissolving the hydroxide in nitric acid. Preliminary experiments with iron containing known amounts of nickel showed that this method could be relied upon to remove traces of the latter element, although the complete elimination of large amounts is relatively slow. It is to be noted that, since the atomic weights of cobalt and nickel are so close to that of iron, the effect of a very considerable percentage of cobaltous or nickelous bromide in the ferrous bromide would be small.

The next step was to dissolve the ferric hydroxide in re-distilled sulphuric acid and to reduce the iron electrolytically from the ferric to the ferrous state. This was done with a large platinum dish as cathode, and a platinum spiral of small surface as anode. The solution of ferric sulphate was concentrated in the first place, so that on cooling the reduced solution ferrous sulphate crystallised out. After removal of the crystals the electrolysis was continued and another crop of crystals obtained. By repeating these operations several times, almost all the iron was eventually recovered as ferrous sulphate. Metallic iron was then deposited electrolytically upon a platinum dish from a concentrated solution of re-crystallised ammonium oxalate. During this electrolysis no manganese dioxide was deposited upon the anode, showing that the material was essentially free from this element. The metallic deposit was thoroughly washed with water and dissolved in the purest nitric acid. A small insoluble residue of carbon remained, which was removed by filtration through asbestos in a filtering apparatus consisting of only quartz and platinum. The asbestos had been digested for some time with aqua regia to remove soluble matter, and thoroughly washed with water. During the crystallisation of the ferrous sulphate and the electrolytic deposition of the metal, aluminium and chromium, as well as alkali metals and silica, must have been eliminated. Further treatment of this specimen was exactly similar to that of sample B.

Ferrous Bromide.—Ferrous bromide was made by dissolving the different preparations of pure iron in the constant-boiling solution of hydrobromic acid in a quartz dish. The acid was freshly distilled through a quartz condenser, and was collected in a quartz vessel. Although the reduction of the ferric oxide to metal was probably more or less incomplete, all three specimens of iron gave clear solutions. At first, the solution of the iron was carried on inside a large desiccator filled with very pure hydrogen, and by means of an electrical heater constructed with platinum wire inside the desiccator the solution was evaporated to crystallisation. The crystals were rapidly removed from the solution and centrifugally drained in platinum Gooch crucibles. Although a portion of the material oxidised to ferric bromide in this operation, the large preponderance of ferrous salts effectually prevented solution of platinum. The crystals of ferrous bromide were then re-crystallised in a similar manner from constant-boiling hydrobromic acid in a quartz dish, and after centrifugal drainage were preserved in a quartz dish in a desiccator containing sticks of potassium hydroxide. Sample A of ferrous bromide was prepared in this way from Sample A of iron.

Sample B of ferrous bromide was made from Sample B of iron in essentially the same way except that during the preparation of this sample it was found more convenient to dissolve the iron in hydrobromic acid in the air on an electric stove as rapidly as possible and to crystallise in the air. Although some oxidation unavoidably takes place, the greater portion of the ferric salt passes into the mother-liquors. Since during the subsequent preparation of the ferrous bromide for weighing, all ferric salt is decomposed, slight oxidation is of no consequence. Sample B of ferrous

bromide was three times crystallised from hydrobromic acid solution.

Sample C₁ of ferrous bromide was made from Sample C of iron in the same way and was crystallised five times from hydrobromic acid. Sample C₂ was obtained from the mother-liquors of Sample C₁, after evaporation and reduction with metallic iron, and was crystallised five times. Sample C₃ resembled Sample C₁, except that the hydrobromic acid solution of ferrous bromide was filtered through asbestos in the platinum-quartz filtering tube, and then the salt was crystallised four times. The asbestos was digested with constant-boiling hydrobromic acid solution before use.

(To be continued).

A METHOD FOR THE DETERMINATION OF TIN IN CANNED FOODS.*

By HERMAN SCHREIBER and W. C. TABER.

THE determination of tin in canned foods, which has recently become of increased importance, may be made by several methods, each having its advantages and defects. Ashing the material at a very low heat in a muffle will give correct results with some foods under some circumstances, but not always, and when the composition of the material is not known, it is not safe to apply this method. Moreover, tin and its salts are volatilised by heat in the presence of chloride of ammonia, and probably with other chlorides also, since it is well known that sodium chloride volatilises on heating strongly. When small amounts of a metal are to be recovered from a large amount of organic matter, the danger of mechanical loss in the fumes is very great. After ashing, the ash must be fused with caustic alkali if all of the tin is to be recovered, so that this process does not offer any advantage over the method herein proposed in regard to the time necessary for making the determination.

Munson has proposed carbonising the organic matter with sulphuric acid and heat, and ashing in a muffle with the aid of nitric acid (*Bull.* 107, Revised, p. 62, U.S. Dept. Agr., Bureau of Chemistry). Determinations made by this method did not give satisfactory duplicates, and the results represented only about 50 per cent of the tin present, as determined by sulphuric acid digestion (Table I.) in Halenke's wet ashing method, as modified by Schryver (Report 7 of the Local Government Board, Medical Department, of Great Britain on the presence of tin in certain canned goods). In the latter method the organic matter is destroyed by digestion with large amounts of sulphuric acid with the aid of potassium sulphate.

TABLE I.—Comparison of the Munson Method and the Sulphuric Acid or Wet Combustion Method (Schryver).

Sample.	Grm. of tin found in 50 grms. of sample.	
	By Munson method.	By sulphuric acid method (Schryver).
Herring in tomato sauce..	0.0236	0.0458
" " ..	0.0217	0.0652
Sardines	{ 0.0318 } 0.0462	0.0652
" " " " " "	{ 0.0682 (a) } 0.0801 (a)	—

(a) Wet combustion not made, given to show poor concordance of results.

Table II. shows that the results obtained when the precipitates are weighed as stannic oxide (SnO₂) are as correct as when the precipitate is dissolved and determined electrolytically as tin (*Bull.* 107, Revised, p. 69, U.S.

* United States Department of Agriculture, Bureau of Chemistry, Circular No. 67.

Dept. Agr., Bureau of Chemistry). Schryver has shown that the wet combustion method gives accurate results and good duplicates. This is also shown by the determinations given in Table II. However, this method has some very serious practical defects. When tin is to be determined in meat, fish, or syrups, only 25 grms. of material can be digested in one flask. This necessitates making two digestions in order that an amount can be used which will avoid the great multiplication of the analytical error which would occur if the result were calculated as mgrms. per kilogram. Using such small quantities of the sample increases the error of weighing and sampling, and, moreover, limits the amount of work which can be done under ordinary conditions. The flasks have a tendency to break during the digestion, which, together with the foaming of the material, requires constant attention and considerable experience before satisfactory results can be obtained. No attempt was made to determine the amount of tin which could be recovered by the various methods by adding known amounts of soluble tin salts to food, since this would not give conditions analogous to those met in practice.

TABLE II.—Comparison of Results by Wet Combustion or Sulphuric Acid Method and by Electrolysis.

Sample.	Wet combustion method (grm.).	Stannic oxide dissolved and re-determined by electrolysis (grm.).
Blackberry jam	{ 0.0126 } { 0.0128 }	0.0124
Herring	0.0325	0.0346
Herring in tomato sauce	0.0296	0.0304
Herring in bouillon . . .	0.0464	0.0468

Our work indicated that the following was the most satisfactory method of making a sulphuric acid digestion:—Weigh 25 grms. of fish or meat, or 50 grms. of vegetables, into a beaker, wash into an 800 or 1000 cc. Kjeldahl flask, add from 100 to 150 cc. of water, 25 grms. of potassium sulphate, 50 cc. of sulphuric acid (sp. gr. 1.84), and a few glass beads. Place over a small flame, rotate a few times till it boils, then increase heat, and boil vigorously until the water is boiled off and fumes of sulphur trioxide appear in the neck of the flask and settle back; remove it from the flame before it foams, or caking will ensue and the flask break in subsequent boiling. Add 50 cc. of sulphuric acid (sp. gr. 1.84), turn the flame down so that it just touches the flask, and heat gently until the mass boils quietly. Again increase the heat, and boil vigorously until decolorised. If the flask is placed in an asbestos ring, cracking can often be avoided. This digestion requires at least six hours.

To determine the accuracy of duplicate determinations by the sulphuric acid method, samples of canned fish were very carefully prepared by passing them through a sausage grinder, and then thoroughly mixing them by hand. From these mixtures duplicate weighings of 25 grms. were made on an analytical balance to ± 0.05 grm., and the following results were obtained:—

TABLE III.—Duplicate Determinations of Tin by the Sulphuric Acid or Wet Combustion Method.

Sample.	Grm. of tin in 25 grms. of sample.	
Composite fish—		
Sample A	0.0134	0.0138
Sample B	0.0079	0.0087
Sample C	0.0164	0.0158

To determine the effect of the presence of sodium chloride on results obtained by the wet combustion method, 10 grms of salt were added to the material to be analysed. The figures given in Table IV. prove that this had no effect on the results.

TABLE IV.—Determination of Tin by the Sulphuric Acid Method in the presence of Salt.

(Grm. of tin in 50 grms. of sample).

Sample.	50 grms. of sample + 10 grms. of salt.	Original sample.
Fish	0.0363	0.0339
Beets	0.0425	0.0419
Peas	0.0282	0.0254

If tin is to be estimated in foods, such as fish, which contain so great an amount of salt as not to be edible before soaking, it is better to determine the tin by the sulphuric acid method, as large amounts of salt would interfere with the burning off of the carbon by the proposed method. However, such cases would be very rare, as salt fish are commonly packed in wood and not in tin.

The method proposed below requires practically no experience in its manipulation, and a large amount of the sample is used, in both of which points it is superior to the wet combustion method. It was at first thought that the destruction of the organic matter could be effected by an alkaline fusion, using alkaline hydrate and nitrates. However, when material, such as fish, which contains fat, is to be analysed, it is impossible to make such a fusion, as it will burn and blow out of the crucible. When alkaline hydrates are used alone, a solid cake results which retards the complete destruction of carbon by coating the small particles. A mixture of hydrate, carbonate, and magnesium oxide was found to give a very porous fusion, in which the carbon was easily oxidised in the muffle. The fusion was at first attempted in large nickel crucibles with very good results, as shown by Table V.

TABLE V.—Comparison of the Sulphuric Acid or Wet Combustion Method with Alkali Fusion in a Nickel Crucible by the proposed Method.

(Grm. of tin per 50 grms. of sample).

Sample	Wet combustion method.	Proposed method, using a nickel crucible.
Herring tomato sauce No. 3552	0.0397	{ 0.0400 } { 0.0383 }
Herring tomato sauce No. 3553	0.0325	{ 0.0351 } { 0.0334 }
Pineapple No. 4876	0.0102	{ 0.0110 } { 0.0101 }

The nickel crucibles, however, were very seriously attacked, and since they are expensive, it was thought that fusion in an iron crucible would be a great advantage on account of the lower cost and the higher melting-point of iron. When iron crucibles were first substituted, the results obtained were lower than by the wet combustion method, and a repetition of the determination gave no solution of the difficulty. At this time hydrochloric acid was used for dissolving the fusions, and finally, on the theory that the trouble was due to the solvent action of the iron chloride on the tin, sulphuric acid was substituted for hydrochloric acid, and correct results were obtained, as shown in Table VI.

The results reported in Tables IV. to VII. were obtained in the preliminary work done in developing the proposed method. In the method, as then used, 5 grms. of magnesium oxide were employed, and the solution of the fusion was not concentrated until it fumed with sulphuric acid, but was simply boiled down, and blue ribbon paper was used for the first filtration. It was found that the fusions could be burned at a lower temperature if 10 grms. of magnesium oxide were used, which makes the burning much easier and materially lengthens the life of the crucible. It was also found best to use a larger amount of acid, as specified in the method, since under certain circumstances all of the tin was not dissolved when only 50 cc. of 1:1 sulphuric acid and 5 cc. of nitric acid were used. The use

TABLE VI.—Comparison of Results by the Wet Combustion Method and the proposed Method, using Different Solvents and an Iron Crucible.

(Grm. of tin in 50 grms. of sample).

Sample.	Wet combustion method.	Proposed method.	
		Using hydrochloric acid.	Using sulphuric and nitric acids.
Beets . .	0.0419	0.0331	{ 0.0416 0.0403 } 0.0410
Tomatoes .	0.0345	0.0290	{ 0.0331 0.0310 } 0.0320
Peas . .	0.0254	0.0252	{ 0.0283 0.0268 } 0.0276
Corn . .	0.0277	0.0238	— —
Apples . .	0.0338	0.0239	{ 0.0320 0.0343 } 0.0332
Spinach . .	0.0048	0.0060	— —
Mushrooms	0.0107	0.0147	— —
Canned fish	0.0325	—	{ 0.0298 0.0328 } 0.0313

of blue ribbon paper was also abandoned, since it decreased the speed of filtration, and, furthermore, it has no apparent advantage (Table VII.) when the precipitation is made as specified in the proposed method. The experimental data indicate that sulphuric acid alone will not take all of the tin into solution, although no explanation of this can be offered.

TABLE VII.—Comparison of Results by the Wet Combustion Method and proposed Method using Blue Ribbon Filter-papers and Sulphuric Acid.

(Grm. of tin in 50 grms. of sample).

Sample.	Wet combustion method.	Proposed method, using blue ribbon filter-papers (·) for the first filtration and 50 cc. of 1:1 sulphuric acid and 5 cc. of nitric acid to dissolve the fusion.	
Beets . .	0.0419	{ 0.0403 0.0424 }	0.0414
Peas . .	0.0254	{ 0.0265 0.0275 }	0.0270
Corn . .	0.0277	{ 0.0269 0.0276 }	0.0273
Apples . .	0.0338	—	0.0323
Fish . .	0.0325	{ 0.0303 0.0329 }	0.0316

(a) These tin oxides were only very slightly discoloured, being very nearly the same shade as those from the wet combustion.

The proposed method has several advantages over the wet combustion method:—(1) It decreases the errors of sampling; (2) it decreases the errors due to multiplication when calculating to mgrms. per kilogram; (3) there need be no loss of samples if the material is properly ground and not heated too rapidly on the hot plate; (4) in the wet ashing methods it is necessary to neutralise a large amount of acid before precipitating with hydrogen sulphide.

Molasses and heavy syrups must be dried longer on the hot plate than any other material analysed, over three hours being necessary to dry these properly. However, as it requires no attention at this stage, this is not a serious defect as compared with the difficulties of determining tin by the wet ashing method. In drying any material on the hot plate it is not necessary to dry it down to a hard crust if it is put in a cold muffle and heat applied gradually. If tin is to be determined in oils, less of the sample should be used, so that there will be an excess of free sodium hydrate. The sulphuric acid method for the determination of tin cannot be applied to oils, and therefore no comparison of the two methods can be made.

The Proposed Alkali Fusion Method.

Pass the sample through a meat-grinding machine, and mix the resulting mass well so as to get as homogeneous a sample as possible. Weigh 100 grms. of the sample and 10 grms. of magnesium oxide into an 8-ounce wrought-iron crucible on a rough balance. Add 50 cc. of an aqueous solution containing 150 grms. of sodium hydrate and 100 grms. of sodium carbonate per litre, stir well with a short piece of stout glass rod, add 75 cc. of 95 per cent alcohol, and stir again. Place on the steam-bath, and evaporate the alcohol. This must be done with care, stirring frequently at the beginning, else it may bump or foam over, but if the material is gradually heated there is no danger of loss. If the material foams, remove from the steam-bath or hot plate for a moment, and then replace on the bath, and it will usually boil quietly. Large lumps in the mass will cause bumping; therefore the sample should be as fine as possible. Fish liquefy on the steam-bath, boil down quietly, and without bumping. After danger from frothing has ceased, apply the full heat of the steam-bath. This evaporation requires about one hour. Transfer to a hot plate covered with a thin sheet of asbestos, and dry down gradually, running at from 130° to 160° C. at first (determine temperature by laying a thermometer on the asbestos); then raise the temperature and continue the boiling, finally using the full heat of the hot plate, which should be sufficient to boil off sulphuric acid. This requires from one and a-half to two hours. Place in a cold muffle, heat gradually until all volatile matter is driven off, and then burn until all of the carbon is destroyed. This requires from two to three hours. Remove from the muffle as soon as burned, cool, cover the residue with water, and let stand a few minutes. Using an iron spatula, scrape and wash the contents of the crucible into a 600 cc. beaker. Cover the beaker, and add gradually 40 cc. of dilute sulphuric acid (1:1) and 10 cc. to the crucible containing some water. Rotate, scrape the sides of the crucible with a spatula, and wash into the beaker. When the reaction is ended, add 50 cc. of sulphuric acid (sp. gr., 1.84) and 30 cc. of nitric acid (sp. gr., 1.42). Cover with a watch-glass, and boil briskly on a hot plate, finally with the full heat of the hot plate, until the residue gives off fumes of SO₃. Allow to fume for ten minutes, remove from the hot plate, and allow to cool but not to solidify. Pass the stem of a funnel bent at an angle over the lip of a beaker and under the cover glass, and add successively small amounts of distilled water through the funnel from a wash-bottle until violent action has ceased. Then add rapidly about 150 to 200 cc. more water through the funnel and remove the funnel and watch-glass, washing into the beaker with distilled water. Stir the cake in the beaker, and wash into a 1-litre Erlenmeyer with distilled water.

The total volume in the Erlenmeyer at this time should be about 300 to 400 cc. Cool, pass in hydrogen sulphide for a few seconds, rotate the flask, and add 28 per cent ammonium hydroxide slowly until the black colour of the precipitated iron sulphide just persists on rotating the flask. Immediately make acid with 1:1 sulphuric acid, and add 10 cc. excess of the dilute acid. Dilute the contents of the flask to 1 litre with boiling water, and continue passing in a rapid stream of hydrogen sulphide for twenty-five minutes more, cork, and let stand over-night. The next morning heat on the steam-bath for about half-an-hour, rotating the flask two or three times during the heating, partly cool by setting in cold water, so that the flask can be handled easily, and filter on to a 12.5 cm. ashless white ribbon paper, No. 589, washing the filter with a solution consisting of 50 cc. of glacial acetic acid and 100 cc. of a saturated solution of ammonium acetate, made up to a litre with distilled water. Wash the precipitate six times with this solution, filling the filter at each washing. Return the filter-paper and precipitate to the Erlenmeyer, add 100 cc. of 20 per cent potassium hydroxide, and boil over a free flame for a couple of minutes until the filter paper is broken up and the solution is clear. (The flask can be manipulated over the flame easily with a large wooden

test-tube holder made of strips of pine-wood and rubber bands). Immediately decant through a double white ribbon filter-paper of 12.5 cm. into a 400 cc. beaker, washing the flask and filter with successive portions of hot water until the filtrate comes through colourless. The filtrate will have a volume of about 200 to 300 cc. Add 20 cc. of concentrated hydrochloric acid to this solution, stir, add a few drops of phenolphthalein, and add concentrated hydrochloric acid from a burette until the dark colour of the solution disappears, then add 1 cc. excess of the acid. Test with a strip of litmus, and see that the solution is acid, stir well, place on a steam bath, heat for twenty minutes, cover, and let stand over-night.

In the morning test the supernatant liquor, which should be perfectly clear and brilliant, with a piece of blue litmus. If not acid, make so with concentrated hydrochloric acid, and then add an excess of 1 cc. If the supernatant liquor is acid and turbid, make alkaline with potassium hydroxide and then acid with 1 cc. excess. The solution must neither be alkaline nor too acid, or there will be trouble in filtering and washing. Heat on a steam-bath for half-an-hour, stirring two or three times. Filter on to a 12.5 cm. white ribbon paper. The precipitate will sometimes run through, and must be returned until the filtrate is perfectly clear and brilliant. If the solution to be filtered is stirred vigorously, allowed to stand until the precipitate clots, and then poured on to the filter, re-filtering may usually be avoided. The filtrate must be perfectly clear or some tin will be lost. Wash alternately with distilled water and the ammonium acetate solution previously mentioned until the filtrate obtained from a washing with distilled water is free from chlorides. (Do not mistake the precipitate given by the acetate solution and silver nitrate, which is soluble in water, for silver chloride). This requires washing until the volume of the filtrate is 200 cc. or more. Fill the filter at each washing. Place the moist filter in a porcelain crucible, dry, and char on an asbestos gauze, and burn off all carbon over the free flame. Cool in a desiccator, and weigh as stannic oxide.

Table VIII. gives a comparison of the results obtained by this method and those obtained by Schryver's method.

TABLE VIII.—Comparison of proposed Method with Schryver's Sulphuric Acid Method.

(Grm. of tin in 100 grms. of sample).

Sample.	Proposed alkali fusion method.	Schryver's sulphuric acid method.
Mushrooms	{ 0.0385 0.0366 0.0355 }	0.0368
Herring in tomato sauce	0.0682 (a)	0.0664
Apples	0.0700 (a)	0.0676
Beets	{ 0.0859 0.0847 0.0662 }	0.0853
Tomatoes	{ 0.0697 0.0679 0.0679 }	0.0698
"	0.0210 (a)	0.0204
Herring in bouillon ..	0.0959 (a)	0.1008
Kipperd herring	{ 0.0336 0.0299 }	0.0317
Composite samples of fish—		
Sample A	0.0508 (a)	0.0544
Sample B	{ 0.0338 0.0386 0.0638 }	0.0363
Sample C	{ 0.0615 0.0627 }	0.0644

(a) Duplicates not run, as there was not sufficient material.

Experiments were made to determine the relative value of potassium hydrate and ammonium sulphide as solvents for tin sulphide, and it was found that they gave concordant results. In one instance, the solution by potassium hydrate gave 0.0313 grm. of stannic oxide, and the

ammonium sulphide gave 0.0318 grm. The sample of ketchup on which these determinations were made contained a large amount of sand, and the results show that there is no danger of silica contaminating the stannic oxide when potassium hydroxide is used. Copper was found in some of the foods examined, and since copper sulphide is more soluble in ammonium sulphide than in potassium hydrate, it seemed advisable to use the latter.

A muffle 9 by 21 inches will hold 10 crucibles at a time, and one analyst can easily make 20 determinations in a week. If the heating in the muffle is gradual and the crucibles are removed as soon as all of the carbon is destroyed, the crucible will not be blistered on the outside and only slightly on the inside, and can be used for repeated fusions. If the crucibles have been spun with a copper or brass tool, the traces of copper adhering to the crucible should be filed off. Fifteen determinations can be weighed, dried, and burned in nine hours, using a hot plate 14 by 18 inches, and a muffle 9 by 21 inches. This requires three hours' continuous watching, and then only an occasional inspection of the muffle and changing the position of the crucibles. Straight ashing, on the other hand, requires at least seven hours' burning in the muffle if even approximately accurate results are to be obtained, and if the food can be put into the muffle without previous drying.

Two hundred and fifty determinations were made in working out the details of this proposed method.

ELECTROLYTIC DETERMINATION OF COPPER.

Edited by F. W. TRAPHAGEN.

ALMOST without exception, the electrolytic method is the one used for all shipment and settlement assays on copper products.

The following methods are those worked out by the chemical staff of the Anaconda Copper Mining Co., and will be found generally available for the materials described.

Allow about 0.11 ampère for each determination. With the present arrangements in the electrolytic room (103 volt lighting circuit) this gives a tension of from 1.40 to 2.30 volts.

In all cases a drop of the electrolyte is brought in contact with a drop of H₂S water on a spot plate to test if copper has been completely deposited.

The platinum cylinders with deposited copper are washed in water, then alcohol, dried on a steam-bath, and weighed.

If deposited copper is dark from presence of arsenic, it is dissolved in 8 cc. HNO₃, diluted with water, and electrolysed again, care being taken to remove solution from the battery soon after the complete deposition of the Cu.

Copper may be separated from Bi, Sb, and As by precipitation as sulphocyanide, the precipitate washed thoroughly, ignited gently in porcelain crucible, dissolved in 7 cc. of HNO₃, and Cu determined electrolytically.

In samples containing As, Sb, Te, and Se, such as electrolytic slimes, add 100 mgrms. of Fe to the HNO₃ solution of sample from which silver has been removed as chloride. Add ammonia to precipitate Fe and still have solution acid.

Bring to boil, settle, filter off Fe precipitate; re-dissolve and precipitate as before. A third precipitation may be necessary to be certain of having all Cu in the solution.

Combine filtrates and electrolyse. The Fe precipitate holds the As, Sb, Se, and Te.

Converter Copper.—Dissolve ½ grm. in 8 cc. HNO₃, 8 cc. water, and 1 cc. H₂SO₄, keeping covered during solution. When solution is complete and fumes expelled, fill beaker with water and place on battery.

In the Cu determinations on mattes and converter copper the percentage of silver, as determined by fire

assay is deducted from percentage of Cu + Ag found by electrolysis. (291.66 oz. = 1.00 per cent). The Ag may be precipitated with just sufficient dilute NaCl, care being taken to avoid an excess. The silver chloride is filtered off, and the Cu alone deposited by the current.

Mattes.—Moisten 1 grm. sample with a few drops of water, add 8 cc. HNO_3 and 1 cc. H_2SO_4 . Take to dryness on steam-bath. Take up with water and 8 cc. HNO_3 . Filter and place on battery.

Slags.—Decompose 2 grms. in platinum dish with 8 cc. HNO_3 , 8 cc. HF, and 1 to 2 cc. H_2SO_4 . Evaporate to SO_3 fumes. Take up with water and 10 cc. HNO_3 . Place on battery.

Sulphide Ores.—Weigh 1 grm. of sample into a beaker ($3\frac{1}{2}$ in. high and $2\frac{1}{2}$ in. in diameter). Add 8 cc. HNO_3 and a little KClO_3 . Take to complete dryness on steam-bath.

Take up with water and from 6 to 10 cc. HNO_3 . Fill beaker with water, let settle, then place on battery.

Oxidised Ore.—Use 1 grm. sample. Take to dryness with 8 cc. HNO_3 . Add 10 cc. HCl and 2 cc. H_2SO_4 , and take to SO_3 fumes. Take up with 8 cc. HNO_3 and water, let settle, and place on battery.—*Western Chemist and Metallurgist*.

NOTE ON THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS.

By W. O. WALKER and J. A. McRAE.

To Stefanov's method for the determination of halogens in organic compounds (*Ber.*, 1906, xxxix., 4056), which is based on the reducing action of nascent hydrogen, formed by the action of sodium on ethyl alcohol, Bacon (*Journ. Am. Chem. Soc.*, 1909, xxxi., 49) proposed a considerable modification in the procedure by which he uses the action of sodium ethylate on the halogen compounds. We tried this modified method using monobromobenzene and α -bromonaphthalene, both of which were carefully purified. For monobromobenzene the calculated percentage of bromide is 50.93. A Carius determination on the sample we used yielded 50.83 per cent Br. With Bacon's method about forty trials were made, all of the results being low, and in no case were duplicates obtained which agreed, which showed that the reduction was incomplete and irregular. The results for α -bromonaphthalene were low also, but much nearer the calculated percentage. We thought that perhaps an increase in the amount of nascent hydrogen might effect a complete reduction, so 1, 2, 2, 3 times the amounts of sodium and alcohol recommended by Bacon were used. The results obtained with monobromobenzene were 35.36, 50.96, 48.65, 49.19, 49.40, 47.43, 47.18 per cent Br. It will be noticed that the second result is very near the theoretical, but we were unable to get a similar result again.

The sodium used was Merck's, and the alcohol 99.5 per cent.

In acidifying with nitric acid we noticed that if an excess were used a vigorous reaction occurred with the production of nitrous fumes, and the liquid was changed to a greenish yellow colour, which persisted even if boiled. The compounds produced affected the end point in two ways—(1) the ferric thiocyanate seemed to become reduced, with the result that more potassium thiocyanate had to be added, thus lowering the result for bromine; (2) the end point was harder to judge. This difficulty, however, is easily eliminated by acidifying only slightly.

We are forced to conclude, therefore, that this method is not of general applicability, and especially cannot be used with difficultly reducible substances.

Since the above work was done, C. H. Maryott (*CHEMICAL NEWS*, Jan. 6, 1911; *Am. Journ. Sci.*, 1910, xxx., 378) published the results of his work on Stefanov's original method. His results appear similar to ours on

Bacon's modified method. He found, however, that potassium gave good results. He did not try Bacon's modified method.—*Journal of the American Chemical Society*, xxxiii., No. 4.

THE FÉRY REFRACTOMETER.

MESSRS. Adam Hilger, of Camden Road, N.W., have introduced a direct reading refractometer for taking the refractive index for sodium light of oils; solutions of acids; mixtures of glycerin, alcohols, &c., with water; sugar solutions; and other liquids of interest to the industrial chemist. The knowledge of the refractive index of a liquid is of the greatest interest to the chemist, affording as it does on the theoretical side valuable indications as to chemical structure, and on the practical side information as to purity.

The advantages of the instrument are:—

- (1) It reads direct the refractive index of any transparent liquid with a uniform accuracy of nearly 0.0001.
- (2) The glass with which the liquid comes into contact is a crown glass which resists to an exceptional degree the action of chemical reagents.
- (3) The temperature control is extremely simple and effective, and forms an integral part of the apparatus.
- (4) The manipulation of the apparatus is extremely simple and convenient.

M. Ch. Féry has designed this refractometer with special reference to the requirements of chemists. It gives without any calculation whatever, by the simple reading of a vernier, the refractive index of a liquid to an accuracy of nearly one in the fourth decimal place (0.0001). In spite of this high degree of accuracy, which experience has shown to be necessary in certain cases (such as the study of isomeric substances, the adulteration of oils, &c.), the scale of the instrument extends with uniform accuracy from 1.3300 to 1.6700.

But in order that the readings may have a practical value it is not sufficient merely to have an instrument of the requisite sensitiveness, for quite small variations of temperature are of sufficient importance to completely falsify the measurements. Means are therefore provided whereby the small quantity of liquid under test (1 to 2 cc.) can be brought to any particular temperature and there maintained during the measurement.

The scale of the vernier is divided from 1.33 to 1.59, but only the first two decimal places of the refractive indices are engraved in figures on the scale. Each of the large divisions representing 0.01 is divided into four parts, and hence each of the subdivisions represents 0.0025.

The vernier is itself divided into twenty-five parts, so that one reads in the following manner:—

Thirty-nine large divisions plus one small division 0.3925
The vernier division coincides at division 3, indicating 0.0003
Hence the refractive index is 1.3928

The apparatus works between 1.3300 and 1.5326, a setting which is suitable for the majority of liquids of technical interest. If, however, the index of the liquid is not contained within these limits, it is extremely easy to readjust.

The most probable values of the refractive index of pure water at different temperatures, from the researches of Jamin, Hoek and Oudemans, Rühlmann, Fouqué, Lorentz and Prytz, Dufet, Ketteler, Walter, are:—

0°	1.33402
5°	1.33392
10°	1.33373
15°	1.33344
20°	1.33303
25°	1.33255
30°	1.33200

NOTICES OF BOOKS.

The Chemistry of Synthetic Drugs. By PERCY MAY, B.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911. (7s. 6d. net).

THIS book gives a clear account of the properties and constitution of the chief synthetic drugs, and discusses the general physiological effects of various elements and radicles. The chemical changes which drugs undergo in the animal organism are described, and the chief drugs are grouped according to their chemical nature, and their properties and physiological action are treated in some detail. The study of the book should provide a strong incentive to further research work on some types of compounds which are as yet only imperfectly known, and the book is particularly valuable as giving the results of the most recent work on some compounds which have lately come into use in medicine. The references to the literature of the subject are complete, and have been brought down to the latest possible date.

A Systematic Handbook of Volumetric Analysis. By FRANCIS SUTTON, F.I.C., F.C.S. Tenth Edition. London: J. and A. Churchill. 1911. (21s. net).

THERE is no more authoritative work on volumetric analysis in the English language than "Sutton," and the tenth edition will receive all the heartier welcome from chemists and analysts because seven years have elapsed since the ninth was published. The book has been exceptionally thoroughly revised by the author's son, Mr. W. Lincolne Sutton, F.I.C., and Mr. Alfred E. Johnson, B.Sc. (Lond.), F.I.C., A.R.C.Sc.I. They have rigorously cut out all obsolete matter, thus making room for the description of new methods without greatly increasing the size. All recently worked out volumetric processes which can be relied upon to give accurate results are to be found in the book, the alterations and improvements in which are too numerous to be specified in fuller detail. No chemist will regret acting on the recommendation to buy the book, keep it always close at hand, and refer to it constantly.

Chemistry for Beginners. I. Inorganic. By EDWARD HART, Ph.D. Fifth Edition. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. (1.00 dol.).

THE student who learnt chemistry from this book would get only a very superficial knowledge of the subject; the scope is altogether too wide for beginners, and general principles are not sufficiently emphasised. Some of the discussions of theoretical conceptions are utterly inadequate; thus the state of mind of the beginner who read the page on the constitution of matter and studied the formulæ given could, in the most favourable circumstances, be nothing better than chaotic, and, unless he was very carefully supervised by a demonstrator, some of his experimental work would inevitably end in failure; for example, in the first description of the preparation of a gas he is not warned to reject the first portions passing over.

Verhalten des Globulins zu den Sauren—Acidoglobulin. ("Behaviour of Globulin towards Acids—Acidoglobulin.") By Prof. L. MOROCHOWETZ. Moscow: Imprimerie de l'Université Impériale. 1910.

THIS monograph gives a very full account of the chemical nature and reactions of globulin. The history of its investigation is discussed in outline, and the work of chemists who have devoted themselves to the study of it and similar albuminous substances is carefully abstracted. The very full footnotes make the reading of the text rather troublesome, and the student who sets out to read the monograph thoroughly will probably wish that the quotations were fewer and shorter. Descriptions of practical methods of

preparing the compounds of globulin with acids, bases, and salts are included, and a complete bibliography is provided.

Über die Anwendung der Zylinderlinse in Spektralapparaten. ("Use of Cylindrical Lenses in Spectral Apparatus.") By E. GEHRCKE. Berlin: Julius Springer.

IN this reprint from the "Zeitschrift für Instrumentenkunde" for March, 1911, the author explains how the use of a cylindrical lens in spectroscopic apparatus may lead to a considerable improvement in the clearness of the spectral lines. He gives details of how to arrange the lenses in order to obtain the most satisfactory results, the time of exposure being reduced to a fraction of its former duration, and states that an ordinary piece of glass rod of diameter about 5 mm. may be used as a lens, and will increase the sharpness of the lines obtained with a concave grating.

Über das Dopplerspektrum der Wasserstoffkanalstrahlen. ("The Doppler Spectrum of the Hydrogen Canal Rays.") By E. GEHRCKE and O. REICHENHEIM. Braunschweig: Fried. Vieweg und Sohn. 1911.

THE authors of this pamphlet, which is reprinted from the *Transactions of the German Physical Society*, explain in it further details of their hypothesis of the cause of two maxima of distribution of intensity of the Doppler bands in the canal ray spectrum, and in particular discuss Stark's arguments against it, and bring forward fresh evidence to show that the hydrogen atomic and molecular rays receive their velocity from the same accelerating cause.

Über die Spektren der Anodenstrahlen. ("The Spectra of the Anode Rays.") By O. REICHENHEIM. Leipzig: Johann Ambrosius Barth.

IN this article the details of the author's optical investigation of the spectra of the anode rays are given in full, the experimental arrangement of the apparatus being described, and the results of the study of the alkalis, alkaline earths, and some other elements tabulated. In discussing his results and the most satisfactory interpretation of them, the author puts forward Stark's hypothesis as the simplest which takes into account all the phenomena observed.

Manuel Pratique d'Analyse Organique. "Practical Handbook of Organic Analysis". By FRANK E. WESTON. Translated into French from the Second English Edition by P. R. JOURDAIN. Paris: H. Dunod and E. Pinat. 1911.

THE value of this laboratory book of organic chemistry, which gives short and clear directions for the analysis of the commonest organic compounds, is testified to by the translation of it into French, to fill a gap which previously existed in French chemical literature. The translation has been carefully and accurately performed, and the author has added some notes and revised some portions of the work.

Action of Ammonia on Chloraloses.—M. Hanriot and A. Kling.—A solution of ammonia in absolute alcohol replaces an atom of chlorine in *p*-chloralose by an atom of hydrogen. This reaction is general for chloraloses. Thus from α -chloralose the compound $C_8H_{12}Cl_2O_6$ is obtained. Galacto-chloralose behaves in the same way as its isomers derived from dextrose. Dichlorogalacto-chloralose on oxidation does not give the corresponding acid but it hydrolyses, giving galactose. The chloralose containing C_7 derived from arabinose gives the same reaction.—*Comptes Rendus*, clii., No. 23.

CORRESPONDENCE.

USE OF ACETYLENE IN LABORATORIES.

To the Editor of the Chemical News.

SIR,—I wonder if any correspondent will help me over a technical difficulty that has presented itself to me?

My laboratory is situated in the country, some distance from a gas supply, so I have installed acetylene in preference to spirit Bunsens. I find it works very well for general laboratory purposes, except for the two following drawbacks:—

1. After the Bunsen has been alight for a few minutes the flame, although perfectly non-luminous at first, gradually becomes luminous, thus spoiling any incineration one may be doing in a crucible. This, I take it, is due to the polymerisation of the gas passing through the burner tube which has become heated.

2. I find a great difficulty in obtaining a purifying agent which will thoroughly eliminate PH_3 . This does not affect me in most of my work, but it tells in those operations which require a platinum crucible. After using the latter for an ignition, especially with the foot blowpipe, the bottom of the crucible is quite frosted, owing to formation of phosphides of platinum. This can generally be removed by an agate burnisher, but that takes time, and, of course, means a loss of platinum.

I should be greatly obliged for advice on these matters. Possibly some of your readers use acetylene, and after experiencing the same difficulties have overcome them.—I am, &c.,

H. L. THOMAS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 23, June 6, 1911.

Fluorhydrates of Alkali Fluorides.—M. de Forcrand.—The author has investigated the thermic properties of the fluorhydrates of the alkaline fluorides, and finds that sodium is decidedly different from rubidium, caesium, and potassium. As regards heat of solution rubidium is intermediate between potassium and caesium for the acid and neutral fluorides, and the stability diminishes from sodium to caesium, while for the fluorhydrates the stability increases regularly from sodium to caesium. Judging from the heat of formation $\text{NaF} + \text{HF}$ should boil at about 300° and $\text{CsF} + \text{HF}$ at 500° . Caesium and rubidium fluorides can unite with a considerable excess of hydrofluoric acid to give compounds analogous to $\text{KF} \cdot 2\text{HF}$ and $\text{KF} \cdot 3\text{HF}$.

Catalysing Action of Ferric Sulphocyanide.—H. Colin and A. Sénéchal.—In presence of hydrogen peroxide ferric sulphocyanide has an oxidising action on phenols and potassium iodide, but the action is not due only to the presence of iron. Nor is it to be ascribed to the SCN group, for this is destroyed by H_2O_2 . Probably the oxidation is the result of two causes:—(1) The destruction of the SCN group with formation of persulphuric acid. (2) The catalytic action of the iron.

Chromotellurates.—A. Berg.—From a solution containing 1 molecule of potassium bichromate, 1 molecule of telluric acid, and 2 molecules of chromic anhydride, on cooling or evaporation orange crystals of potassium chromotellurate, $4\text{CrO}_3 \cdot \text{TeO}_3 \cdot 2\text{K}_2\text{O}$, separate out. The corresponding ammonium salt is prepared by substituting ammonium bichromate for the potassium bichromate.

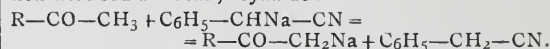
Pyridine Pentachloroiridates.—Marcel Delépine.—The action of chlorine, nitric acid, and aqua regia on the pyridine pentachloroiridates of potassium, sodium, and ammonium gives the corresponding pentachloroiridates from which other analogous salts can be prepared. These salts are very stable towards acids. Both in the iridates and the iridites the pyridine is firmly bound to the iridium.

New Types of Iridoxalic Acids and Complex Iridoxalates.—A. Duffour.—Iridoxalic acid, $[\text{Ir}(\text{C}_2\text{O}_4)_3]\text{H}_3$, can conveniently be prepared by treating triargentate iridoxalate with the equivalent quantity of hydrochloric acid. When the acid is left exposed to the air it changes colour from golden to dark emerald green, a new monobasic iridoxalic acid being formed. The potassium salt of this acid, $[\text{Ir}(\text{C}_2\text{O}_4)_2\text{K} \cdot 5\text{H}_2\text{O}]$, can be obtained by adding 1 molecule of caustic potash to the green liquid. The acid appears to be formed by the reaction—

$$[\text{Ir}(\text{C}_2\text{O}_4)_3]\text{H}_3 + 2\text{H}_2\text{O} \rightleftharpoons [\text{Ir}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]\text{H} + \text{C}_2\text{O}_4\text{H}_2$$

Both the acid and its potassium salt are very unstable, and are easily transformed into a new type of complexes, e.g., $[\text{Ir}(\text{C}_2\text{O}_4)_2(\text{OH})(\text{H}_2\text{O})]\text{K} \cdot 2\text{H}_2\text{O}$, which is the neutral salt of a dibasic hydro-hydroxydioxalo-iridous acid. Crystals of $[\text{Ir}(\text{C}_2\text{O}_4)_2(\text{OH})(\text{H}_2\text{O})]\text{KH} \cdot \text{H}_2\text{O}$ can also be prepared; they are isomeric with the original green salt, except as regards their water of crystallisation, and this is evidently a case of Werner's co-ordination isomerisation.

Action of Acid Chlorides, Acid Anhydrides, and Ketones on the Monosodium Derivative of Benzyl Cyanide.—F. Bodroux.—Acetyl chloride reacts with monosodium benzyl cyanide to give a very poor yield of 2-phenyl-3-butanone-1-nitrile. Benzoyl chloride gives a good yield of 1-2-diphenyl-1-propanone-3-nitrile. Acetones of formula $\text{R}-\text{CO}-\text{CH}_3$ undergo a double decomposition with sodium benzyl cyanide:—



Those of formula $\text{R}-\text{CO}-\text{R}'$, R and R' being aromatic radicals, give the compounds

$$\begin{array}{c} \text{R}-\text{C}=\text{C}-\text{CN} \\ | \\ \text{R}' \text{ C}_6\text{H}_5. \end{array}$$

Ethyl Derivatives of Acetone.—Ernst Zerner.—The action of ethyl iodide on dipropylketone in presence of sodamide gives triethylacetone, from which tetra-, penta-, and hexa-ethyl acetones can be obtained by similar treatment. All these ketones have a smell like that of camphor.

Oxidation of Higher Fatty Acids with Acetylene Function.—A. Arnaud and V. Hasenfratz.—On oxidation with nitric acid the chain between the two CO groups of the diketonic acids is broken; thus stearolic acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$, gives pelargonic and azelaic acids. With permanganate, however, the chain is split into three parts, and one CO group is eliminated as CO_2 .

THE
DAVY-FARADAY RESEARCH LABORATORY
OF
THE ROYAL INSTITUTION.

Director:

Professor SIR JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

Superintendent of the Laboratory:

Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday, for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

LENT TERM.—Monday, January 8, to Saturday, March 30.

EASTER TERM.—Monday, April 22, to Saturday, July 27.

Full information and forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

THE CHEMICAL NEWS.

VOL. CIV., No. 2699.

THULIUM.*

By C. JAMES.

I.

THULIUM was discovered by Clève in 1879 (*Comptes Rendus*, Sept. 1, 1879) while trying to separate the element that gives a rose colour to the salts of "old erbium." The earths used for this investigation consisted of some material obtained by Nilson while working upon ytterbia. These residues were separated during the use of "the fusion of the nitrate method," and consisted of those portions which were less basic than yttrium but more basic than ytterbium.

Clève submitted this crude erbia to another long series of fractionations by again fusing the nitrates. This work yielded more basic, intermediate, and least basic portions. Thalén examined these fractions spectroscopically for Clève, and showed that old erbia consisted of at least three elements. To the more basic part, which accompanied yttria, Clève gave the name holmium, and to the least basic the name thulium, derived from Thulé, the old name of Scandinavia. In this paper the oxide of thulium was said to be of a light rose colour.

Soret (*Comptes Rendus*, Sept. 15, 1879) stated that he had observed differences in the absorption spectrum of various fractions of erbium supplied by him to Marignac, and, in the case of holmium, he had provisionally named this element X, as it appeared almost impossible to separate it. In addition it was well known that certain conditions somewhat modified the spectra.

Lecoq de Boisbaudran (*Comptes Rendus*, Sept. 15, 1879) was of about the same opinion as Soret. However, he maintained that the thulium red band was rather broader than the ordinary red band of erbium.

Clève (*Comptes Rendus*, Aug. 9, 1880) separated more of the oxide and found it to be white, while its solutions in acids gave colourless salts which showed two absorption bands, one in the red and one in the blue, the blue band being broad only when the solutions were very concentrated. This material gave an atomic weight of 170.7.

Thalén (*Comptes Rendus*, Aug. 16, 1880) examined Clève's purest thulium, which, in solution in the form of the nitrate, was nearly colourless. It gave a weak erbium absorption spectrum, brilliant lines belonging to ytterbium, and about 15 new lines due to thulium. He said:—"It seems that a new metal exists, though it must be admitted that it has not yet been separated from ytterbium and erbium."

Lecoq de Boisbaudran (*Comptes Rendus*, Sept. 7, 1885) recorded the presence of thulium in some fractions.

Kruss and Nilson in 1887 (*Ber.*, x2., 2134) concentrated thulium during some of their investigations upon rare earth minerals, so that the absorption bands were stronger than those of erbium. Finding in some solutions that the absorption bands did not show the same relative intensities, they came to the conclusion that thulium consisted of at least two elements—thulium α , the one giving the band λ 684.0, and thulium β , for the one giving the band λ 465.0. It is doubtful whether these chemists realised that concentration, acidity, &c., might modify the spectrum, as had been pointed out by some earlier workers.

Crookes (*CHEMICAL NEWS*, lx., 39), in a paper on the rare earths, described a lot of spectroscopical researches in which a figure for the absorption spectrum of thulium was shown.

Kruss in 1893 (*CHEMICAL NEWS*, lxxviii., 148) obtained some fractions rich in thulium.

Astrid Clève (*Zeit. Anorg. Chem.*, xxxii.; *CHEMICAL NEWS*, lxxxvi., 248), during the preparation of some ytterbium material, supposed that a violet colour of certain fractions of fused nitrates was due to thulium; she also stated that this element was eliminated only with difficulty from ytterbium.

R. Marc (*Zeit. Anorg. Chem.*, xxvii., 304), in a communication on terbium, was of the opinion that thulium was a mixture of ytterbium and yttrium containing varying quantities of holmium and terbium.

C. Auer v. Welsbach (*Monats. Chem.*, xxxvii., pp. 8, 935), describing a new method for the separation of the ytterbium earths, mentioned the fact that thulium concentrated between erbium and ytterbium, the thulium bands being of greatest intensity in the solutions coloured only faintly pink.

About this time the author (*Journ. Am. Chem. Soc.*, xxix., 495; *CHEM. NEWS*, xcvi., 61, 205), working with solutions of the rare earth oxalates in ammonium carbonate, observed that thulium concentrated in the more soluble fractions along with "ytterbium" and some erbium.

Bettendorff (*Liebigs Ann.*, ccclii., 88; and *CHEMICAL NEWS*, xcvi., 249) considered that the rose colour of erbium salts was due to thulium, since he found that the brighter the rose colour the stronger the bands of thulium.

Urbain (*Comptes Rendus*, 1907, cxlv., 759), in describing the separation of the element lutecium, stated that in fractionating old ytterbium thulium separated in the least soluble portions.

The writer (*Journ. Am. Chem. Soc.*, xxx., 182; and *CHEMICAL NEWS*, xcvi., 61), giving a new method for fractionating the rare earths, noticed that thulium could be rapidly concentrated in the bromate fractions between erbium and "ytterbium."

Hoffmann and Burger (*Ber.*, xli., 308), when purifying Nilson and Kruss's erbium, found that dilute ammonium hydroxide removed thulium in addition to the ytterbiums.

Urbain (*Comptes Rendus*, cxlv., 759) mentions the fact that the atomic weight of thulium is not above 168.5.

Extraction.

Since thulium is very rare it is absolutely necessary to commence with very large amounts of material. In this work the following minerals have been employed:—Brazilian monazite (yttrium earths, derived from Brazilian monazite); xenotime; ytterspar (Norwegian xenotime, impure); euxenite; fergusonite (Norway, &c.); ytrotitanite; sipylite (columbate from Northern Norway); gadolinite (Norway and Sweden). Also large amounts of oxalates from more soluble double potassium sulphates from Carolina monazite, supplied by the Welsbach Co. through the kindness of Dr. H. S. Miner.

The best sources were found to be ytterspar, euxenite, and a columbate from an island in the north of Norway. Gadolinite varied very considerably, some varieties being fairly good, while most were rather poor in the erbium earths. Fergusonite contains only a very little of the desired elements. Ytrotitanite is very troublesome to work up. A specimen of samarskite, presented to the author recently by Prof. F. J. Metzger, Columbia University, was found to resemble euxenite with regard to its content of erbium metals. The details of the processes for the extraction of the mixed rare earths from the various minerals are as follows:—

1. *Euxenite*.—The material was very finely ground and mixed with an excess of strong sulphuric acid in iron pots of about two gallons capacity. The mixture was then carefully heated until it frothed considerably, after which it was removed from the furnace and stirred rapidly, when a vigorous reaction took place. As soon as the evolution of gas began to slacken the vessel was replaced in the furnace in such a manner that only hot gases from the fire could play upon it, in order that the sulphuric acid might not

* Abstract given before the New York Section of the American Chemical Society, March 10th, 1911.

evaporate too rapidly. When the mass became hard, the iron pot was moved to a much hotter position, and kept there until the excess of acid had been driven off. The furnace used was capable of taking four of these iron vessels at one time.

When the operation was successful the residue had risen, very much like a cake during the baking process, and when in this condition was very readily removed by means of a hammer and chisel. If the operation were not successful, which was usually the case when the pot was left out too long, the whole settled down to a very hard mass which was only removed with great difficulty, so much so that the cast-iron vessels were often broken. With very little practice the correct conditions were readily established. The decomposed mineral was powdered, placed in a churn containing water, the churn closed, and the contents well agitated.

When the solution was completed the churn was emptied into a tub, and the latter allowed to stand for about twelve hours. After this period had elapsed, the metallic acids were found to have settled so that the clear supernatant liquid could be syphoned off and the rare earths precipitated by means of oxalic acid. The thick mass of columbic acid, &c., remaining at the bottom of the barrel was thrown upon a linen filter, and washed with water. Washing by decantation was also very effective.

Sometimes, when the mineral had not been finely pulverised, the decomposition was not complete. In this case the residue was stirred with water, and allowed to stand for a short time, after which the liquid, still containing the mineral acids in suspension, was run off from the dense undecomposed euxenite. The latter owing to its density rapidly settles. This coarser material was dried, re-ground, and again worked up. The columbic and tantalac acids were allowed to deposit, and the wash-water was employed for the solution of more sulphated mineral.

Earthenware vessels were used for the precipitation. (These can be obtained in various sizes. Those possessing round bottoms can be heated by means of steam or calcium chloride baths).

Fergusonite and Samarskite.—As fergusonite appeared to contain only small amounts of the erbium earths, and since samarskite resembled euxenite, the writer did not operate upon more than several kilograms. The methods used to attack these substances were:—(a) By boiling with sulphuric acid containing some K_2SO_4 so as to increase the temperature; (b) hydrofluoric acid.

When using sulphuric acid and potassium sulphate it was found necessary to stir well during the hardening, as otherwise the whole solidified to a cement-like mass. The result of the reaction after powdering was treated with ice-cold water, filtered, and the clear filtrate precipitated with oxalic acid.

The hydrofluoric acid method was found to be an excellent one, inasmuch as the mineral need not be so finely ground. However, the cost was a great drawback, to obviate which the author prepared the acid on a large scale by using a capacious iron retort fitted with a leaden cover. The condenser consisted of a large lead pipe running through a barrel of water. The top of the condenser was so formed that water could drip in in sufficient quantity to form a concentrated fuming acid.

Columbates.—Some columbates are attacked only with great difficulty by sulphuric and hydrofluoric acids, while they are very rapidly decomposed by means of sodium hydroxide in the fused condition.

The mineral used resembled sipylite. It was much richer, however, in rare earths, since it contained about 43 per cent. (See "Analysis," next column).

This mineral, which was of a reddish brown colour, came from an island in the north of Norway. It possessed endothermic properties, since upon heating it soon began to glow. This glow rapidly passed through the mass. After cooling, it was observed that the mineral had become yellowish, more opaque, and could easily be powdered. Its specific gravity before heating was 5.30, and after

Analysis.

Cb_2O_5 (trace Ta_2O_5)	42.42
SiO_2	4.27
WO_3 , SnO_2	0.37
ZrO_2	0.41
Cu group	1.38
U_3O_8	1.40
Fe_2O_3 , Al_2O_3	1.55
Yttrium earths	39.91
Cerium earths	3.57
ThO_2	1.10
CaO	1.25
MgO	0.07
Loss upon ignition (H_2O , He, &c.)	2.00

99.70

heating 4.62. The atomic weight of the yttrium earths was found to be about 110.2.

The analysis and other determinations were carried out very carefully by Mr. H. P. Corliss, to whom the author wishes to express his thanks.

In order to separate the earths the mineral was first ignited, powdered, mixed with twice its weight of sodium hydroxide, and carefully fused for about two hours. The liquid mass was then poured upon an iron plate. The cold melt was next broken in pieces, and allowed to stand in contact with water until it assumed the appearance of mud. It was then mixed with hot hydrochloric, and the whole heated upon the water-bath.

The columbic acid, &c., was then filtered off, and the rare earths precipitated by means of oxalic acid.

Ytrotitanite.—Hydrochloric acid was used for attacking this substance. The mineral was finely powdered and heated with the acid for a considerable period. The acid liquid was filtered, and the small amount of rare earths present precipitated as the oxalates. A large excess of acid was always avoided.

Ytterspar (Impure Norwegian Xenotime).—The best method for decomposing this mineral was found to be as follows:—

Sodium hydroxide was mixed with a little less than half its weight of water in an iron pot, the temperature raised to the boiling-point, and powdered ytterspar, equal in weight to the sodium hydroxide employed, was added. It was then stirred until the charge solidified, after which the temperature was raised to a low red heat. The result of the reaction was very friable and readily removed from the containing vessel. The crumbled material was mixed with water, boiled, and filtered. The hydroxides, titanic acid, gangue, &c., remaining upon the filter were well washed with boiling water. The green filtrate usually became thick owing to the mass of crystals (phosphates) which separated as the liquid cooled. The hydroxides were treated with a slight excess of hydrochloric acid, the solution was filtered, and the earths separated by the use of oxalic acid.

Gadolinite was decomposed by heating with hydrochloric acid. The earths were obtained in the usual well known way.

As the ytterspar earths contained only a very little of the elements of the cerium group, they were converted directly into the bromates in the following manner:—

The crude oxides, obtained by igniting the oxalates, were dissolved in hydrochloric acid, the solution diluted, filtered, and precipitated by oxalic acid. The oxalates were converted into sulphates by the action of concentrated sulphuric acid. The anhydrous sulphates were dissolved in cold water. The solution was then poured upon barium bromate, covered with a layer of water, and heated upon the water-bath (*Journ. Am. Chem. Soc.*, xxx., 182). When the decomposition was complete the barium sulphate was filtered off, and the bromates fractionally crystallised.

The earths from euxenite, gadolinite, &c., which con-

tained members of the cerium group, were first subjected to the sodium sulphate treatment. (In using sulphate of sodium in place of sulphate of potassium care must be taken not to employ a great excess, otherwise some of the yttrium earths will be precipitated also. Yttrium sodium sulphate is rapidly decreased with regard to its solubility after the concentration of the sodium sulphate has reached a certain point. This problem has been partly studied, and the solubility curve, &c., will be published shortly). After separating the insoluble double sulphates, the solution was precipitated by means of oxalic acid, and the yttrium earth oxides, obtained by igniting the oxalates, were converted into bromates in a similar manner to the crude ytterspar oxides described above.

After the bromates had been fractioned for some time (*Journ. Am. Chem. Soc.*, xxx., 990) it was found that nearly all the erbium had accumulated in the more soluble fractions, nearly all of which were quite free from the absorption bands of holmium and dysprosium. Since terbium was less soluble than dysprosium, and since the oxide had the pure rose tint of erbium, it was evident that the material was quite free from the terbium. The separation of ytterbium and lutecium from erbium was found to be very rapid. Five crystallisations of a mixture of erbium, thulium, ytterbium, and lutecium, which possessed a fine rose colour together with a strong erbium absorption spectrum, left most of the material in the mother-liquor as a colourless liquid. The absorption bands of erbium and thulium were very faint when observed through a saturated solution 5 cm. thick.

Thulium separated fairly rapidly, and collected in the fractions between erbium and ytterbium as the crystallisation was continued. Whenever the thulium bands became intense, the fraction was placed aside until no more would separate from the series. The less soluble fractions consisted of erbium with some yttrium.

The more soluble portion was then taken, and again submitted to fractional crystallisation. This portion was nearly colourless. It showed the absorption bands of thulium together with a very weak spectrum of erbium. It was apparent that by far the greater portion consisted of ytterbium and lutecium, with perhaps traces of scandium. Of this crude material there was nearly 3 kilograms. The work was carried out in a room that possessed a fairly constant temperature of about 60° F. Higher temperatures were not suited for the work since they tended to prevent crystallisation of the more readily soluble fractions. (The bromates must be free from impurities, since metals, which form bromates not isomorphous with the rare earths, cause the formation of tiny crystals, so that it is practically impossible to drain off the mother-liquor). Casseroles were the vessels employed, and the concentration was so gauged that the major portion separated in the crystalline form.

Since the more soluble bromates crystallise rather sluggishly, they were first crystallised once a day. However, when the most soluble portion had been removed two operations could be carried out daily.

Because the salts form supersaturated solutions with extreme ease, it was absolutely necessary to start the crystallisation with a crystal.

During the first few series of operations, erbium rapidly separated, leaving the more soluble portions coloured greenish. As the work proceeded, thulium concentrated in the fractions next to the least soluble erbium. When the mother-liquors were found to be free from thulium they were placed aside. The colour shown by these bromates in solution was of a yellowish green, which was afterwards found to be due to copper. Scandium occurred in these fractions in the merest traces only. This latter element was more inclined to separate with the erbium. This was, perhaps, due to the fact that the solutions became slightly basic. After all copper and other impurities had been removed the fractions, more soluble than thulium, became colourless and formed good crystals.

The most interesting portion of the series was where the thulium accumulated. When free from erbium the solu-

tions possessed a bluish green colour. After sixteen weeks of this stage of the fractionation the colours of the various fractions, from the least soluble to the most soluble, were rose, yellow, bluish green, colourless, and, finally, those coloured yellowish green (copper). The yellow tint was due to admixture of erbium and thulium.

When the fractions became too small to re-crystallise from water, a mixture of alcohol and water was used with good results.

After continuing the work it was observed that the thulium fractions did not change in colour, simply remaining of a greenish tint when in solution. The presence of a very little erbium has a marked influence upon this colour, since a trace turns it yellowish green, a little more renders it colourless, and further addition pink. As the fractionation progressed, it was evident that the alcohol was being slowly attacked by the bromates. This decomposition increased; the liquids became coloured, and smelt strongly of bromine and ethyl acetate. At this point the fractions were united according to colour, and precipitated as the oxalate. The oxalate was of a very pale green tint when moist. Artificial light increased this tint, so that it became a delicate pale green colour. The oxide, obtained by igniting this oxalate, also showed this green tint, and yielded a carmine glow, when heated carefully by a Bunsen burner.

The extraction of thulium, commencing with the crude yttrium earth bromates, will be better understood by the accompanying diagrams.

Some thulium oxide containing ytterbium was dissolved by heating with concentrated nitric acid for a short time, a large excess of concentrated nitric acid was added, and the boiling liquid fractionally precipitated by means of a boiling saturated solution of oxalic acid. Oxalic acid was added until a permanent precipitate formed, when the liquid was well stirred and cooled. The crystalline oxalate was removed by filtration, and the filtrate again heated and treated with more oxalic acid solution, and so on. The final mother-liquor was evaporated nearly to dryness, taken up with water, and all earths thrown out as oxalates.

After a number of series of precipitations had been carried out, some of the oxides from the first and last fractions were dissolved in concentrated hydrochloric acid and the spark spectrum photographed. The negatives obtained showed that there had been practically no fractionation, as the lines were identical in relative intensities.

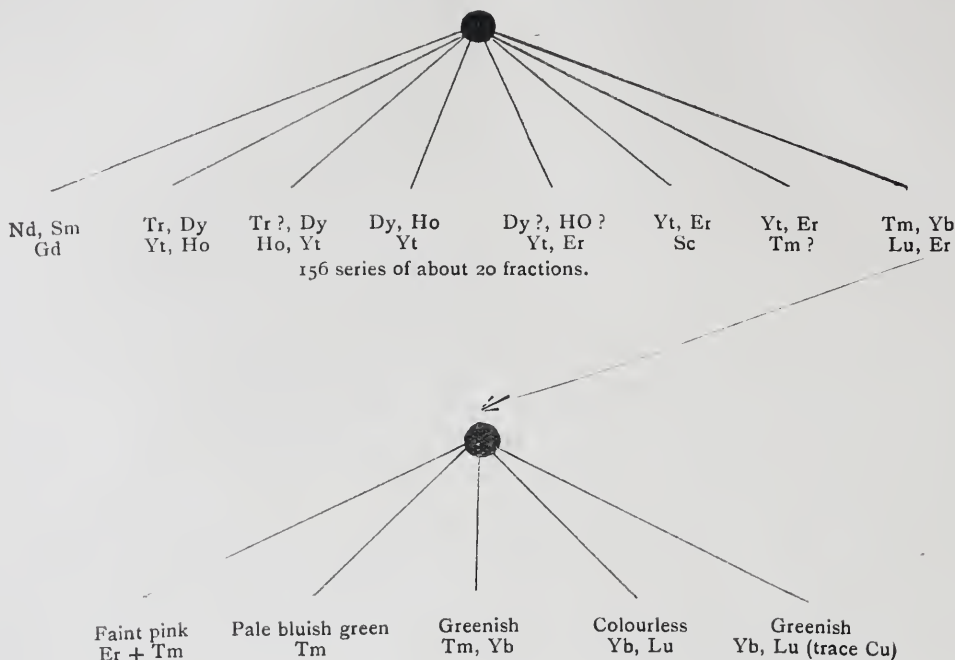
The picrates were next tried. Thulium oxide similar to that used for the previous experiment was converted first into the hydroxide, and then into the picrate. The solution of the picrate was then evaporated and fractionally crystallised. After six series, the first and last fractions were compared by the use of a spectrograph. The photograph showed scarcely any change in the lines.

One of the least soluble thulium bromate fractions, which contained a little erbium, was converted into the oxalate. This oxalate was fractionated by the oxalate carbonate method. The results showed that this procedure was not rapid enough to be of any value.

In addition to these methods several others were tried, but none could be compared with the bromate method.

Since yttrium bromate comes between the bromates of praseodymium and neodymium, with regard to their solubility in water, and because the bromate of praseodymium is more soluble than the corresponding compound of yttrium (*Journ. Am. Chem. Soc.*, xxxi., 913), it was considered that by crystallising a mixture of erbium, thulium, and praseodymium bromates that praseodymium would come between erbium and thulium. An experiment along this line showed that praseodymium rapidly accumulated in the least soluble fraction. However, by gradually feeding this substance through the most soluble fractions, they were kept larger and the erbium was swept out. Owing to the rapidity with which praseodymium separated from erbium, it was thought advisable to try a mixture of the bromates of yttrium and praseodymium carrying small

CRUDE YTTRIUM EARTH BROMATES.



amounts of erbium and neodymium. The results were surprising, as the praseodymium again appeared in the fractions less soluble than yttrium. According to the solubilities, as previously mentioned, yttrium should be more soluble than neodymium but less soluble than praseodymium. The solubilities had been determined at 25°, while the crystallisations had been carried out at room temperature. The solubilities of lanthanum bromate and praseodymium bromate in yttrium bromate solution will be studied at the earliest opportunity.

A specimen of the purest thulium so far obtained by the bromate method was sent to Sir William Crookes, who examined it by means of the spectrograph. He said:—"Spectroscopic analysis shows very good thulium, and a trace of ytterbium. Only a very faint trace of calcium is present." The writer is extremely grateful to Sir William Crookes for his kindness in testing this and many other specimens.

These purest fractions were again converted into the bromate and fractionated first from water solution and then from aqueous alcohol. Later, a mixture of methyl and ethyl alcohols was tried. By employing methyl alcohol in place of water it was hoped that the decomposition of the bromates would be prevented. After working for a short time the liquid became coloured, and a crystalline compound, insoluble in the mixed alcohols, was deposited. This compound was soluble in water, and evolved bromine when acidified with hydrochloric acid.

The various fractions were mixed according to their purity. The purest product being reserved for a determination of the equivalent, which will form the main subject of the next paper on thulium. The fractions not quite so pure were used for the preparation of many compounds, some of which are given below.

The greatest point proved by this work is that the element, giving the characteristic absorption bands of thulium, cannot be separated into simpler substances. After about 15,000 operations the absorption spectrum underwent no change.

Compounds of Thulium.

Thulium Oxide, Tm_2O_3 , prepared by igniting the oxalate. It forms a dense white powder with a faint green tint. This oxide dissolves slowly if heated with strong acids, and when carefully made to incandesce emits a carmine coloured glow.

Thulium hydroxide as usually obtained forms a precipitate which settles very readily, and filters nicely even when thrown down in the cold. This compound dissolves easily in dilute acids.

Thulium Bromate, $\text{Tm}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$, was obtained by decomposing barium bromate, covered with water, and heated upon the water-bath, with a solution of thulium sulphate. As soon as the supernatant liquid failed to give a test for sulphuric acid, the barium sulphate was filtered off, and the filtrate concentrated. As the liquid cooled the salt separated in pale bluish green prisms belonging to the hexagonal system, and isomorphous with the other rare earths.

The bromate was obtained in nice small crystals by pouring a saturated solution into an excess of 95 per cent alcohol. After standing a short time the liquid became full of crystals, which upon analysis gave the following results:—

	Tm_2O_3 .	Br_2O_5 .	H_2O (diff.).
Calculated ($\text{Tm} = 168.5$) ..	26.95	50.37	22.68
Found	27.08	50.34	22.58

Ammonium hydroxide was found to be the best precipitant. The thulium hydroxide must be well ignited, as otherwise the results run a little high. The oxalate gave figures that were slightly low, indicating a tendency of the oxalate to dissolve in dilute acid.

Thulium Chloride, $\text{Tm}_2\text{Cl}_6 \cdot 14\text{H}_2\text{O}$.—Thulium oxide was dissolved in concentrated hydrochloric acid, and the solution evaporated until crystals formed upon the surface. It was then placed in a desiccator over sulphuric acid until a quantity of the chloride had crystallised out. The crystals were pressed between thick filter-paper under a press.

The nearly dry chloride was finally freed from moisture over sulphuric acid. This compound, which possessed a green tint, was very soluble in water and alcohol. When 0.4 grm. was dissolved in 100 cc., a distinct absorption band in the red could be seen using a layer 5 cm. thick.

Analysis:—

		Tm_2O_3 .
Calculated..	..	48.06
Found ..	..	48.26

Thulium Sulphate, $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.—In order to obtain this salt some oxide was dissolved in a slight excess of hydrochloric acid. The solution was diluted somewhat, an excess of sulphuric acid added, and the whole poured into an excess of 95 per cent alcohol. The resulting product was very milky, and after a few minutes crystals began to form. When it had stood for some time the sulphate settled. It was filtered off and washed with alcohol to remove all traces of hydrochloric and sulphuric acids. The anhydrous sulphate was easily obtained by carefully heating the hydrated compound nearly to redness. When the anhydrous compound was added to water it formed a sticky mass at the bottom of the beaker, which, however, rapidly dissolved. The neutral sulphate solution seemed to be more astringent, but less sweet, than a corresponding solution of ytterbium.

The hydrated sulphate gave 18.80 per cent H_2O , and the anhydrous salt 61.52 per cent Tm_2O_3 , upon analysis. These results show that the amount of water of crystallisation is similar to most of the other rare earth sulphates, viz., $8\text{H}_2\text{O}$.

Thulium Oxalate, $\text{Tm}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, is obtained as a white precipitate with a greenish tint by treating a slightly acid solution of thulium with a solution of oxalic acid. Using hot solutions an oxalate was prepared possessing the following composition:—

	Tm_2O_3 .	C_2O_8 .	H_2O (diff.).
Calculated ..	54.30	30.46	15.24
Found ..	54.20	30.35	15.45

This salt is soluble in potassium and ammonium oxalates owing to the formation of double salts. These double oxalates have been used by Auer von Welsbach for separating the members of the yttrium group. The author found this procedure to be more troublesome and very much slower than the bromates.

Thulium Acetylacetonate,



This compound was prepared by precipitating a solution of thulium chloride by an excess of ammonium hydroxide, washing the precipitate first by decantation, then on a Buchner funnel, and finally dissolving the hydroxide in a warm mixture of absolute alcohol and acetylacetone. Thulium hydroxide dissolved with great ease in the above mixture. On evaporating the solution the salt separated. This was purified by re-crystallising from absolute alcohol. It was not volatile in a vacuum.

The acetylacetonate gave 40.02 per cent Tm_2O_3 upon ignition, which indicates that there are two molecules of water of crystallisation present.

Some thulium material carrying a little ytterbium (neoytterbium) was converted into the acetylacetonate and submitted to several series of fractional crystallisations. The most soluble and least soluble portions showed a slight difference in the spectrograph. Unfortunately this compound readily undergoes hydrolysis, and for this reason it cannot be used for purifying thulium.

The absorption spectrum of an alcoholic solution of the acetylacetonate differs from aqueous solution of other salts, such as the nitrate and chloride. The difference is shown more especially by the blue band, which in the case of the acetylacetonate is most intense on the side towards the red, whereas the nitrate in aqueous solution gives the most intense part on the violet side.

Thulium Phenoxyacetate,



Thulium hydroxide was dissolved in a solution of phenoxyacetic acid in dilute alcohol. The clear liquid was evaporated, the crystals were separated upon a Hirsch funnel, and washed with water. The crystalline mass was well stirred with 95 per cent alcohol, after which an equal volume of ether was added. The phenoxyacetate was again filtered and washed with ether. This compound is very voluminous, sparingly soluble in water, and soluble in alcohol. By a simple ignition it was found that the thulium oxide amounted to 28.58 per cent.

Thulium Nitrate, $\text{Tm}_2(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$.—This was obtained by dissolving thulium oxide in nitric acid and evaporating to small bulk. After a slight excess of fuming nitric acid had been added, the nitrate crystallised out. This compound is deliquescent. When it was dried over sulphuric acid and analysed it gave the following results:— $\text{Tm}_2\text{O}_3 = 45.24$ per cent; calculated, $\text{Tm}_2\text{O}_3 = 45.12$. This compound, therefore, contains eight molecules of water of crystallisation. Most of the rare earth nitrates contain ten or twelve molecules of water. Thulium nitrate resembles "old ytterbium" nitrate, since Astrid Clève gave $8\text{H}_2\text{O}$ as the amount of hydration of the latter salt.

Thulium nitrate can readily be crystallised from nitric acid. The fractionation of the simple nitrates from nitric acid was first proposed by Demarcay, and since then has been used with great success by Urbain. At this end of the series the nitrates are very soluble, and strong nitric acid must be used during the fractional crystallisation.

Durham, N.H.

ON THE BEHAVIOUR OF FUSED SILICA AT HIGH TEMPERATURES.*

By A. BLACKIE, B.A., Assistant at the National Physical Laboratory.

IN view of the large number of uses to which vitreous silica is now put, it may perhaps be of some interest if a short account is given of some investigations concerning its behaviour at high temperatures which were made at the National Physical Laboratory three years ago, and which have not hitherto been published. The tests were made at the request of the Thermal Syndicate, Ltd., of Newcastle-on-Tyne, and the results mentioned in this paper are published by their kind permission.

The research had the following objects:—

1. To ascertain the loss of strength of the substance after heating to high temperatures for definite periods.
2. To examine the changes in the structure of the material which take place under the same conditions, and—
3. To compare the coefficients of expansion of the transparent and opaque varieties.

For the purpose of the first two investigations the laboratory was supplied with samples of four different types of vitreous silica of convenient sizes. When necessary these were cut or ground to the correct dimensions.

(NOTE.—When necessary the silica was cut by means of a horizontal mild steel disc armed with diamond or carborundum dust. The diameter of the wheel was about $8\frac{1}{2}$ in. and its thickness rather less than 1.32nd inch. It was electrically driven, and proved very satisfactory, it being possible to cut quite large and thin sections by this means. Some interesting phenomena concerning the re-arming of the disc were noticed during the course of the research. Grinding and polishing were carried out by means of carborundum wheels and discs covered with carborundum papers of different grades, and where necessary the specimens were finished on the usual buffs.)

* A paper read before the Faraday Society, May 23, 1911.

Vitreous silica may be obtained in two main types:—

(a) As a transparent glass almost or quite free from bubbles. This is prepared by a difficult and lengthy process, but when finished is as clear as good glass.

(b) As an opaque or translucent glass containing bubbles. The difficulty of manufacture is in this case not so great, and very much larger apparatus can be made. In most cases, unless transparency be an object, it may be used for the same purposes as the transparent material.

The types of silica used in this research may be briefly described as follows, and are subsequently referred to by letters. The first three types are opaque or translucent:—

Silica "U" (Unglazed).—This material was received in the form of rods which had been drawn and then cut into thinner strips. It shows long parallel-sided bubbles.

Silica "G" (Glazed).—These specimens have been subsequently glazed on both surfaces. The inner, intermediate, and surface layers show quite distinct types of bubbles.

Silica "S" (Satin-like).—These specimens had one smooth surface with a satin-like sheen, showing flat elliptical bubbles, while the other surface was rough and had a few adhering grains of sand.

Silica "T" (Transparent).—This was transparent and glass-like, and showed a few long parallel-sided bubbles. The specimens were formed by collapsing the walls of tubes by means of heat until flat sides were obtained.

1. Strength Tests.

The test selected as a criterion of the strength of the materials was the transverse fracture of a beam. The tests were carried out on batches of samples some of which had been subjected to the action of heat for definite periods. Each batch consisted of specimens of the various types, and in all cases these were heated and cooled together under precisely similar circumstances.

The testing arrangement consisted of two steel blocks resting on a surface plate and kept at a constant distance, 1.5 cm., apart. Above these is a steel beam pivoted at one end, and bearing immediately above the centre of the gap between the blocks an ebonite knife edge, by means of which the load was applied. (Ebonite was employed in order to prevent the "gritting" action of a sharp metal edge on the silica. The edge lasted surprisingly well, although the pressures were quite considerable). The force was applied to the free end of the beam by means of a tension screw connected by a cord to a spring balance which measured the force applied directly. The specimens for test varied from 1 to 3 mm. thick and from 5 to 10 mm. wide, and were measured carefully both before and after fracture.

The criterion chosen for the strength of the beam is the quantity known as the modulus of transverse fracture, and is defined as $f = \frac{6M}{bh^2}$, where M is the maximum bending

moment and b and h the width and depth of the beam respectively. Tests on specimens of different thicknesses and of the same kind showed a sufficiently good agreement with this law to warrant its use in reducing figures for comparative purposes.

To obtain the value of f for any particular class of material about ten similarly treated specimens of various thicknesses were broken, and the result for each reduced according to this formula. The mean of all was taken as the value of f . Considering the nature of the material it was not deemed safe to trust to a smaller number of experiments for each figure. The probable error of the mean was in each case ascertained.

After the tests of the different materials in the virgin state, samples of each kind were heated together in a platinum wound electric furnace for different periods and temperatures, and were afterwards tested for strength. The samples were placed in the furnace, which was raised as rapidly as possible to the desired temperature, and then maintained steady for the requisite number of hours, and

allowed to cool naturally before the specimens were removed. A continuous photographic record of the temperature was taken throughout, and it was found easy to maintain the latter constant throughout the run within a few degrees. The specimens were tied in bundles with platinum wire, on which they rested, and were subject to the action of the air while being heated.

The two fragments of each specimen after breaking (the great majority broke cleanly under the knife edge) were preserved, and the most typical were subsequently utilised for the preparation of the specimens for the microscopic examination of the second part of this research.

The following is an abstract of a table giving the value of f in kilograms per square cm. for most of the tests made. In most cases the probable error is from 10 to 20 units except in the case of silica "T," where it is somewhat larger:—

Mean furnace temperature.	Period of heating (hours).	Strength in kilos/cm.².			
		U (unglazed).	G (glazed).	S (satin-like).	T (transparent).
Unheated	—	342	382	281	902
1124° C.	8	376	310	319	818
1122°	3½ + 4½	358	337	307	750
1188°	4	425	309	285	897
1186°	8	309	311	277	802
1275°	4	257	270	211	745
1353°	4	218	186	188	339

On comparing the relative strengths of different kinds of silica as shown in this table, it is at once noticeable that the transparent material is between two and three times as strong as the others at all temperatures. Of the latter, material "S" seems to be the weakest and material "U" the strongest, although "G" in the unheated state shows greater strength.

Material "U" (Unglazed).—This material, though showing a slightly smaller strength than "G" when unheated, shows an interesting behaviour on heating. It would appear that the first effect of heating is to increase the strength through some kind of annealing action. Thus after eight hours at 1124° a ten per cent increase is shown. This action becomes much quicker at a very slightly higher temperature, an increase of over 25 per cent being shown after four hours' heating at 1188°. It, however, seems to be accompanied by the usual devitrification, which increases with the time during which the specimen is exposed to the high temperature; thus after eight hours at 1186° the strength is not so great, being only 8 per cent in excess of that of the virgin material.

Heating for a period of four hours at 1275°, the devitrification becomes serious and the strength is decreased by 25 per cent, while four hours at 1353° decrease it by 36 per cent. (Some tests were made on pieces of microscope slide glass, some of which were annealed for a few hours at temperatures just below their softening point. Their strength was found to have increased by about 25 per cent, although traces of devitrification were already showing).

Material "G" (Glazed).—This shows a greater average strength in the virgin state than "U" or "S," although the material in this condition seems less reliable, as the values obtained for f were distributed over a wider range and the consistency figure was in consequence lower. This material shows a continuous drop in strength when heated, but gives better values for consistency after heating than before. It fact, it may be looked upon as a material which has had its natural strength artificially increased by the glazing process, its internal structure probably being strained in some way. Probably, however, it is released from this condition when raised for some time to a higher temperature. The decrease after eight hours at 1124° is between 10 per cent and 20 per cent, while four hours at 1188° seem to produce much the same effect; nor do eight hours at this temperature appear to produce further change. The probable explanation is that devitrification has scarcely assumed an important part, but that the loss of strength is due to the relief of the strained state due to the glazing.

After heating for four hours at 1275°C ., however, a further decrease of strength of 30 per cent from the virgin state is shown, while four hours at 1353° reduce the strength by 50 per cent.

Material "S" (Satin-like).—This shows a low strength in the unheated condition and a slight increase of 10 per cent on heating for eight hours to 1124° . Four hours' heating at 1188° are enough to bring it back to the original value, while eight hours do not seem to alter this value appreciably. In this matter it behaves similarly to the glazed material. Four hours at 1275° decrease its strength by 25 per cent, while four hours at 1353° reduce it by 40 per cent.

Material "T" (Transparent).—This material, showing a much greater strength than the other, also proved more difficult to test. It showed a decrease of strength of 9 per cent after heating for eight hours to 1124° . When this was carried out in two shorter periods a greater decrease was shown. At 1188° four hours' heating show no change, while eight hours reduce the strength by 10 per cent. These observations seem to show that, although the loss of strength is not great, it is more dependent on time than on temperature, for in the case where the heating at 1122° was broken into two periods, owing to the double time taken in heating up and cooling, the specimens were subjected to high temperatures for a longer period than in the direct eight hours' run. Four hours' heating at 1275° , however, show an unmistakable decrease of 17 per cent, while four hours at 1353° show a decrease of over 60 per cent, reducing the strength of the transparent silica to only half as much again as that of the other kinds tested. Two or three of the specimens showed flat devitrified cores after heating to the higher temperatures. This was probably due to the original inner surface of the tube from which the specimen was made.

Summary and Conclusion.—We may summarise the more certain of the above results as follows:—

1. That the transparent silica is at all stages much stronger than the other kinds.
2. That the glazed silica is slightly stronger than the other two kinds in the virgin condition, but loses its advantage on heating.
3. That the satin-like silica is slightly the weakest.
4. That the unglazed silica has the property of showing increase of strength when heated to 1188° for four hours, but that the process of devitrification subsequently overcomes this.
5. That in general loss of strength hardly commences at 1120° , at 1188° it exists but is not very serious even after eight hours, but that four hours at 1353° makes a reduction of 40–60 per cent, thus showing that the rate of loss of strength increases very rapidly as the temperature rises.

2. Microscopical Examination.

Subsequently to the strength tests a microscopical examination of the specimens was carried out, using polarised light. The specimens were prepared and examined in the same way as rock sections, though owing to the transparency of the substance the extreme order of thinness usually required was not found to be necessary.

It is not necessary in the present paper to describe all the phenomena observed, which are of greater interest to mineralogists, but the following general conclusions, which are more or less applicable to all types of the silica, may be mentioned. They are:—

General Conclusions.—1. That except for a few small grains of quartz and an occasional grain of carborundum from grinding, no foreign nuclei were observed, and that the former were only occasionally starting-points for crystallisation.

2. That at the lower temperatures to which the substance was heated, crystal growth was confined to the outer surface and the walls of bubbles, especially of those open at the ends and near the surface of the section.

3. That sometimes at 1275° , and nearly always at 1353° , crystals were formed in the ground mass and a micro-

crystalline structure developed in some areas. It is possible that this may be partly attributable to some small traces of impurity in a state of solid solution. Silica "T" did not show this apart from bubbles.

4. That the crystal formed consisted of tridymite.
5. That they are very minute, but increase slightly in size to about 1118° , and then usually become shattered at higher temperatures.
6. That the changes in mechanical strength very closely follow the crystalline changes.
7. That the formation of the crystals seems to be accelerated by contact with the air or in parts of the specimen which may become permeable to air, the inside of the specimens usually being attacked last.
8. That above the transition point of vitreous silica to tridymite the change can probably not be prevented entirely.

It may be mentioned that as far as the work was on the same lines as that of Day and Shepherd on the Lime-Silica series of minerals, it was confirmatory of their results.

(To be continued)

A REVISION OF THE ATOMIC WEIGHT OF IRON.*

THIRD PAPER.—THE ANALYSIS OF FERROUS BROMIDE.

By GREGORY PAUL BAXTER,
THORBERGUR THORVALDSON, and VICTOR COBB.

(Continued from p. 66).

3. Preparation of Ferrous Bromide for Analysis.

As in the analysis of many other metallic bromides in this laboratory, the ferrous bromide was prepared for weighing by fusion in a current of nitrogen and hydrobromic acid gases. In the earlier work upon ferrous bromide fusion was unnecessary, since the salt was prepared by sublimation in a current of dry gases, and therefore contained only superficial moisture and ferric salt which could be eliminated by heating at a temperature below the fusing-point. In the present instance, however, the salt contained at least four molecules of crystal water and possibly included ferric bromide. While in several recent investigations it has been found possible to expel crystal water from hydrated crystals almost completely by heating them to a temperature at which they effloresce without melting, traces of moisture seem to be invariably retained (Baxter and Tilley, *Journ. Am. Chem. Soc.*, 1909, xxxi., 210; Baxter and Chapin, *Proc. Am. Acad.*, 1910, xlvii., 237; *Journ. Am. Chem. Soc.*, xxxiii., 21). The desirability of fusing the ferrous bromide was therefore evident. Several difficulties were met in carrying out this operation. In the first place, in several preliminary experiments where the bromide was fused in a current of nitrogen and hydrobromic acid gases in a platinum boat, a superficial alloy of iron and platinum was formed. Whether this was due to dissociation of the salt or to the presence of a small proportion of hydrogen in the nitrogen was not determined. A similar difficulty met by Baxter and Coffin in the fusion of cobaltous chloride in a current of pure hydrochloric acid gas leads one to believe that the former explanation is the real one (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1584). The only other material available for containing the salt during fusion was fused quartz. Fortunately experiments showed that ferrous bromide could be fused in a boat of this material in an atmosphere containing hydrobromic acid gas without attacking the quartz boat appreciably and without decomposition of the salt.

The second difficulty lay in the preparation of pure hydrobromic acid gas. In most previous investigations in this laboratory the method which has been used is to saturate nitrogen gas with bromine, and then to pass the mixture through concentrated hydrobromic acid solution

* From the *Journal of the American Chemical Society*, xxxiii., No.

containing red phosphorus. Both before the hydrobromic acid solution becomes saturated with the gas and after a considerable amount of phosphorous acid has accumulated in the solution, volatile phosphorus compounds are likely to accompany the mixture of nitrogen and hydrobromic acid gases (Baxter, *Proc. Am. Acad.*, 1903, xxxix., 247), even if they are thoroughly scrubbed in a series of U-tubes containing saturated hydrobromic acid solution. This method was therefore used only in three of the preliminary experiments.

The method employed by Richards and Hönigschmidt in the fusion of calcium bromide (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1583), that of saturating hydrogen with bromine and passing it over hot platinum, is unsuited to the case of ferrous bromide on account of the occasional large excess of hydrogen in the hydrobromic acid gas.

A more satisfactory method was found in charging the nitrogen with hydrobromic acid gas by passing it through fuming hydrobromic acid solution. In this way all possibility of contamination with phosphorus was avoided.

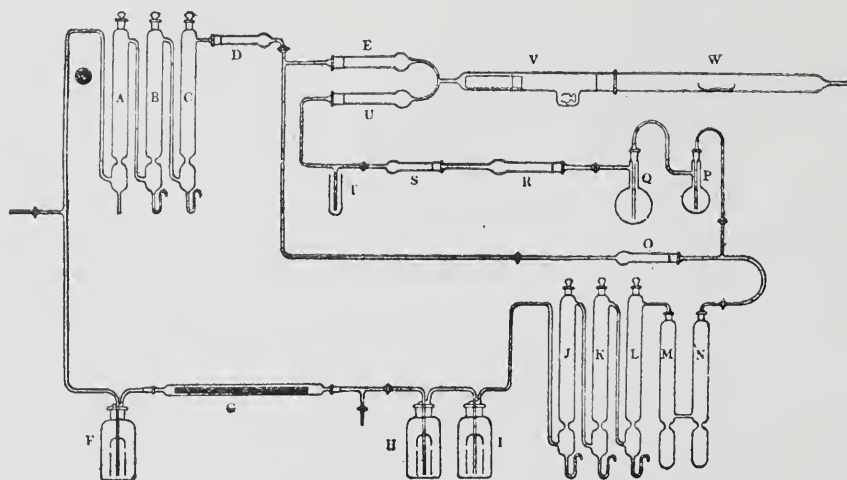
The apparatus for preparing the various gases was as follows:—Nitrogen was obtained by passing air through concentrated ammonia solution in the bottle F (see Fig.) and then over hot copper gauze in the hard-glass tube G. The excess of ammonia was removed by dilute sulphuric acid in the bottles H and I. The gas was then conducted

was passed a second time over fused calcium bromide in the tube U. The fuming hydrobromic acid solution contained ferrous bromide to prevent the evolution of bromine.

When desired the nitrogen could be passed directly through the phosphorus pentoxide tubes, O and E, into the bottling apparatus VW in which the fusion took place. Air was purified and dried by passing over silver nitrate in the tower A, fused potassium hydroxide in the tower B, concentrated sulphuric acid in the tower C, and phosphorus pentoxide in the tubes D and E.

All connections in the apparatus were made of fused or ground glass. No lubricant whatever was used on the ground joints and stopcocks which came in contact with hydrobromic acid, but these joints were so long and so well ground that there could have been no diffusion inward. Either concentrated sulphuric acid or Ramsay desiccator grease was used for lubrication in the nitrogen and air apparatus.

In the final drying of the hydrobromic acid phosphorus pentoxide was not used on account of the danger of the formation of volatile phosphorus compounds (Baxter, Hines, and Frevet, *Journ. Am. Chem. Soc.*, 1906, xxviii., 779). Calcium bromide was chosen for this purpose, because its first hydrate has a very low aqueous pressure, 0.2 mm. at 25°, i.e., 1 litre of moist gas passed over fused calcium bromide retains only 0.0002 gram of moisture (from results



through a tower, J, filled with beads moistened with silver nitrate solution, two similar towers, K and L, containing dilute sulphuric acid to eliminate last traces of ammonia, and two towers, M and N, filled with sticks of fused potassium hydroxide to absorb carbon dioxide and moisture. In the first three experiments the partially dried gas, after bubbling through bromine in a small flask, passed into a second flask containing concentrated hydrobromic acid solution in which carefully washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid solution, removed traces of bromine, which escaped reduction in the flask. Two additional U-tubes, containing beads moistened with concentrated hydrobromic acid solution only, served to eliminate volatile phosphorus compounds. Finally the mixture of nitrogen and hydrobromic acid gases was thoroughly dried by means of fused calcium bromide.

In all except the first three experiments the nitrogen was charged with hydrobromic acid gas by bubbling through fuming hydrobromic acid solution in the bulbs P and Q. The mixture was dried by means of fused calcium bromide in the tube R, and, after being freed from a possible trace of bromine by anhydrous ferrous bromide in the tube S,

by Baxter and Warren, published in *Journ. Am. Chem. Soc.*, xxxiii., 342). The aqueous tension changes very slightly with the temperature. Furthermore, this salt is easily prepared. Fused zinc bromide is a less efficient drying agent. The aqueous pressure of its lowest hydrate is 1.2 mm. at 25°, and increases rather rapidly with the temperature (*Journ. Am. Chem. Soc.*, xxxiii., 342).

The ferrous bromide contained in the weighed quartz boat was placed in the heating tube W of the bottling apparatus (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxii., 59), and after air had been expelled by nitrogen and then by a mixture of nitrogen and hydrobromic acid gases, the tube was gradually heated until the water of crystallisation began to evaporate rapidly (at about 200°, Dammer, *Handb. Anorg. Chem.*, iv., 761). There was never any appearance of melting at this point. As soon as dehydration appeared to be complete the temperature was still further raised until the ferrous bromide fused. The salt was allowed to solidify, and while cooling the mixture of nitrogen and hydrobromic acid gases was replaced by nitrogen, and this in turn by dry air when the tube was cold. While the tube was being swept out with nitrogen and air, a portion of the current of gas was sent backward through the tube U and the trap T in order to avoid all possibility

of contamination with hydrobromic acid. Finally the boat was pushed into the weighing bottle contained in the socket of the bottling apparatus, and the stopper was inserted, all in the current of pure dry air. Several hours' standing in a desiccator near the balance always preceded the weighing of the bottle with its contents. In the preliminary series of experiments the fusion tube was of hard glass, but in the final series of experiments this was replaced by a tube of transparent fused quartz. This quartz tube remained essentially unattacked during the final series of experiments. The tube was electrically heated by means of a removable mica sleeve wound with "Nichrome" resistance ribbon.

4. Method of Analysis.

The procedure for the determination of the bromine in ferrous bromide was essentially that already frequently employed in the analysis of bromides in this laboratory. A solution of the salt was titrated against a weighed very nearly equivalent amount of silver, and then the precipitated silver bromide was collected and determined gravimetrically. However, owing to the reducing effect of ferrous solutions upon solutions of silver salts, preliminary oxidation of the ferrous iron to the ferric state was found necessary in the earlier research upon ferrous bromide.

The salt was dissolved in about 200 cc. of pure water containing two drops of re-distilled sulphuric acid. The acid was necessary, since ferrous bromide dissolved in pure water alone oxidises rapidly and gives a copious precipitate of basic salt. After dilution to at least 600 cc. in a three-litre glass-stoppered precipitating flask, a solution was added containing 99 per cent of the amount of thrice crystallised potassium dichromate necessary to complete the oxidation and 5 per cent more than the theoretical amount of distilled sulphuric acid. In order to avoid loss of bromine by evaporation from the surface of the solution the dichromate was introduced through a funnel with a fine tip reaching to the bottom of the liquid. The solutions were allowed to mix largely by diffusion, aided by occasional very gentle agitation, and the flask was kept closed for some time after the introduction of the dichromate. When the oxidation is effected in this way, absolutely no evidence of free bromine can be obtained in the atmosphere above the solution, although we found experimentally that less than 0.01 mgrm. of bromine could easily be detected by the odour in an empty 3-litre flask.

Very nearly the exact amount of the purest silver to combine with the ferrous bromide was weighed out and dissolved in re-distilled nitric acid which had been diluted with an equal volume of water in a flask provided with a column of bulbs to catch possible splatterings. The solution was further diluted and heated until free from nitrous acid, and then was again diluted until not more concentrated than tenth-normal. This solution was next added to the ferrous bromide solution, which also had been diluted until more dilute than tenth-normal. After thorough mixing by shaking the flask with its contents was allowed to stand for several days with occasional shaking until the supernatant liquid seemed perfectly clear. The solution was then tested for an excess of bromide or silver in a nephelometer with careful observance of all the precautions necessary in the use of this instrument (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235; 1906, xxxv., 510). If a deficiency in either bromide or silver was observed, a suitable amount of a thousandth-normal solution of sodium bromide or silver nitrate was added, and the shaking and testing were repeated. This process was continued until the amounts of bromide and silver were equivalent. The test portions, since they contained only negligible amounts of silver and bromine, were discarded.

In order to determine whether appreciable occlusion had taken place in Analyses 9 and 25, and 13 and 27, the precipitates were allowed to stand in contact with their mother-liquors for three and two weeks respectively after the end-point had apparently been reached. No change in end-point with the time could be detected. In Analyses 13 and 27, moreover, the precipitation was carried out in

the reverse fashion by adding the bromide solution to the silver solution. The results of these analyses were no different from those of the others. Further evidence that no occlusion took place is furnished by the ratio of silver to silver bromide (see *prox.*).

After the exact end-point had been reached in each analysis, an excess of about 6 centigrams. of silver nitrate was added, and the flask was again thoroughly shaken. When the supernatant liquid was clear, the precipitate was thoroughly washed with pure water and collected upon a Gooch-Munroe-Neubauer crucible which had been heated to constant weight at 170° in an electric oven. The crucible and contents were heated for about fifteen hours at the same temperature in the electric oven before being weighed. The greater part of the silver bromide was transferred to a porcelain crucible and the residual moisture was estimated by determining the loss in weight upon fusion. With two exceptions the fused silver bromide was light yellow and transparent. In these two analyses red particles of some iron compound were visible in the bromide, and the results of these analyses were lower than those of the others. These two analyses are omitted from the table of results.

The precipitating flask was carefully rinsed with ammonia, and the silver bromide content of the solution was compared nephelometrically with known bromide solutions. The quantity found in this way was always less than one-tenth of a milligram.

While silver bromide is essentially insoluble in a solution containing a bromide or a silver salt, it dissolves slightly in pure water. The first few washings, owing to the excess of silver nitrate in the filtrate, undoubtedly did not dissolve an appreciable amount of the bromide. Even the later washings, amounting to about 1 litre, could hardly have become saturated with bromide. The correction actually applied in each analysis for solubility of the silver bromide, 0.0001 gram. per litre, certainly can not be far from the correct one. (Böttger finds the solubility to be 0.00008 gram. per litre at 20°, *Zeit. Phys. Chem.*, 1903, xlv., 602; Kohlrausch gives the value 0.00011 at 21°, *Ibid.*, 1905, I., 356).

(To be continued).

A VOLUMETRIC METHOD FOR ANTIMONY IN ALLOYS.

By GEORGE S. JAMIESON.

THE object of this paper is to describe an application of L. W. Andrews' iodate method to the determination of antimony in alloys (*Journ. Am. Chem. Soc.*, 1903, xxv., 756), particularly "hard leads" and solders. The method is satisfactory because it is not interfered with by copper and iron, metals which frequently occur in small quantities in these alloys, and because it is rapid and accurate.

Two other iodometric methods have been compared with this by the writer with less satisfactory results. The first, which is based upon getting the antimony into the pentavalent form in dilute hydrochloric acid solution, adding potassium iodide, and titrating with sodium thiosulphate, gave good results in the absence of copper and iron, but was unsatisfactory in the presence of these metals. The other method, depending upon getting the antimony into the trivalent state in a sodium bicarbonate solution and titrating with iodine, was found to give poor results, particularly with alloys containing much lead, as even when tartaric acid is used, the lead carbonate precipitate appears to hold antimony, thus causing low results.

Andrews showed (*loc. cit.*) that his iodate method was satisfactory for antimony by applying it to pure tartar emetic. The method has been further tested by the writer by dissolving weighed quantities of Kahlbaum's pure antimony in concentrated sulphuric acid and titrating it as described beyond. It is to be observed that this titration is carried out in the presence of 15–20 per cent of actual hydrochloric acid, which gives iodine mono-

chloride as the end-product, according to the equation $2\text{SbCl}_3 + \text{KIO}_3 + 6\text{HCl} = 2\text{SbCl}_5 + \text{KCl} + \text{ICl} + 3\text{H}_2\text{O}$. The potassium iodate solution which was used throughout the entire investigation contained 3.5667 grms. of KIO_3 per litre, corresponding to 0.00400 grm. of antimony for 1 cc.

The following results were obtained:—

Sb taken (grm.).	KIO_3 used.	Sb found.
0.1000	24.85	0.0994
0.1000	24.90	0.0996
0.0490	12.20	0.0488

The following method of analysis for alloys has been worked out:—Take 0.5 grm. of alloy in the form of drillings or chips in a 200 cc. Erlenmeyer flask. (If the alloy contains less than 2 per cent of antimony it is better to take 1 grm. or more, while with alloys very rich in antimony 0.1 or 0.2 grm. will suffice). Add 10 cc. of concentrated sulphuric acid and heat until the alloy is entirely decomposed. (If the flask is covered with an inverted porcelain crucible cover the dissolving and boiling may be carried out without the escape of any disagreeable quantities of fumes, so that the hood need not be used). Boil the solution gently for about two minutes after the lead sulphate has become white, allow the solution to cool to room temperature, dilute with 15 cc. of cold water, allow to cool somewhat, add 15 cc. of 1:1 hydrochloric acid, shake thoroughly, and filter off the lead sulphate on a Gooch crucible, washing with small quantities of the same hydrochloric acid. Transfer the filtrate to a glass stoppered bottle of about 250 cc. capacity, add 5 cc. chloroform, 15 cc. of concentrated hydrochloric acid (to allow for dilution with the standard solution), and 5 cc. of iodine monochloride solution. (To prepare this solution dissolve 10 grms. of potassium iodide and 6.44 grms. of potassium iodate in 75 cc. of water, add 75 cc. of concentrated hydrochloric acid, then add a globule of chloroform in a glass stoppered bottle, and adjust exactly to a faint iodine colour by shaking and adding dilute potassium iodide or potassium iodate solution as the case may require). Shake the titration bottle, let it stand for about five minutes, and then titrate the liberated iodine with standard potassium iodate solution until the chloroform is just decolorised after thorough shaking, which should be repeated in about a minute to make sure of getting the true end-point. (If the volume of potassium iodate solution used is much over 15 cc. it is advisable to add more concentrated hydrochloric acid to keep the strength near the 1:1 point). To make a second titration most of the liquid may be poured off, leaving the chloroform ready for use.

It should be observed that, as Andrews has shown (*loc. cit.*), the strength of the hydrochloric acid solution in which the titration is made is of much importance. The directions, therefore, as given above should be closely followed in regard to the strength and amounts of hydrochloric acid used.

The following results were obtained with a number of alloys:—

No.	Weight taken.	cc. KIO_3 used.	Per cent of Sb.	Per cent of Sb by thiosulphate method.
1A.	0.2000	6.70	13.40	13.43
2A.	0.2000	6.70	13.40	—
1B.	0.2000	6.00	12.00	12.07
2B.	0.2005	6.03	12.03	—
1C.	1.0000	2.70	1.08	1.04
2C.	1.0000	2.70	1.08	—
1D.	0.5000	5.90	4.72	5.11 (a)
2D.	0.5000	5.90	4.72	—
1E.	1.0000	2.40	0.96	0.96
1F.	0.5000	2.85	2.28	2.32
2F.	0.5000	2.85	2.28	—
1G.	1.0000	2.80	1.12	1.16

(a) Solder D contained a little copper or iron which caused the thiosulphate method to give high results. Also alloys A and B were found to contain traces of copper.

The first two alloys are antimonial leads and the others are commercial solders, some of which were of poor quality on account of the antimony present.

The time required for an analysis was about an hour.

Arsenic is rarely present in appreciable quantities in the alloys under consideration, but it is to be noticed that, if present, it would be titrated with the antimony. The following results were obtained by dissolving metallic arsenic in concentrated sulphuric acid and proceeding exactly according to the method that has been given.

As taken (grm.).	KIO_3 used (cc.).	As found.
0.0100	4.10	0.0102
0.0100	4.10	0.0102
0.1019	40.60	0.1015

In a case where an alloy contains an appreciable amount of arsenic it is best to carry out the process exactly as directed as far as filtering off the lead sulphate and washing it with 1:1 hydrochloric acid. Then pass in hydrogen sulphide to precipitate the arsenic, pass air through the liquid for half-an-hour or so to remove the hydrogen sulphide and to oxidise any iron that may be present, filter, wash with 1:1 hydrochloric acid, and titrate as usual. This process was tested by the use of alloys mixed with known quantities of pure metallic arsenic with the following results:—

Alloy taken. Grm.	As taken. Grm.	Per cent. Sb found.	Per cent. Sb in alloy.
0.5000	0.0050	4.72	4.72
0.9560	0.0118	4.77	4.72
0.2000	0.0460	12.00	12.00
0.2000	0.0520	12.10	12.00
1.0000	0.0097	1.04	1.08

—*Journal of Industrial and Engineering Chemistry*, iii., No. 4.

THE DETERMINATION OF ARSENIC AND ANTIMONY IN COPPER.*

By GEORGE L. HEATH.

THIS paper will summarise the principal methods employed in American foundries and refineries, and include a new rapid method for arsenical metal by direct titration of the electrolyte from battery assays, or by titration of a solution of precipitated sulphides of the arsenic group.

The principle of separation of arsenic and antimony from copper is either distillation or gravimetric separation.

Distillation.—Two of the largest laboratories in the United States use some form of this method.

If it is desired to estimate the antimony, as well, by evolution, a mixture made something like the following is used as a distilling solution for decomposition of the sulphides of the arsenic group, which are washed into the still with a little strong hydrochloric acid, completing the extraction from the paper with a few cc. of sodium sulphide solution, or the sulphides can be filtered on a felt which is transferred directly.

(A) Dissolve 150 grms. of chemically pure zinc in 140 cc. of hydrochloric acid (sp. gr. 1.2) and 440 cc. of distilled water, evaporate until the bulk is reduced to about 370 cc. Mix this solution with the solution of 100 grms. of chemically pure cupric chloride, dissolved in 330 cc. of concentrated hydrochloric acid. The total volume of mixed solution = 700 cc.

For slags, &c., take 30 cc., for refined copper 75 cc., of the solution, distil down in the flask which is connected with a short vertical glass condenser, until a thermometer, in the neck of the flask, shows 120° C., then add 35 to 40 cc. additional acid liquid, and distil again. The condenser dips under water in a No. 3 or No. 4 beaker, and

* *Journal of Industrial and Engineering Chemistry*, iii., No. 2.

the distillate is finally removed and titrated with iodine as shown later under the "titration of arsenic."

A clean beaker of water is then placed below the condenser, and the attempt is made, I understand, at two laboratories, to recover antimony by a further distillation at 122° to 160° C.

The antimony may be separated gravimetrically by separating its sulphide from the copper by extraction with dilute sodium sulphide solution (sp. gr. 1.08), and from the trace of tin, which is due to reagents and distilled water, by repeated precipitation and filtration in small volume (25 to 50 cc.) of concentrated oxalic acid.

(B) The iron precipitate, obtained as described under method C, is washed into the Allihn flask, by 100 cc. of strong hydrochloric acid, and then neatly reduced with about 5 cc. of 50 per cent hypophosphorous acid, and distilled at a temperature below 120° C. The condenser dips under water in a No. 3 beaker, and the distillation is repeated with 50 cc. more of the acid. In the writer's opinion, a third distillation should then be made into a beaker of fresh water, which is separately titrated, and the process continued until the distillate shows no more traces of arsenic than one can always expect from the best acid.

Fifty cc. of concentrated zinc chloride solution are then added (W. H. Bassett's method), and the distillation continued at a temperature above 122° C. to evolve the antimony.

In the writer's experience, this distillation process is uncertain, and requires repeated treatments to be sufficiently accurate for refined metal. The following gravimetric methods, accordingly, are to be preferred:—

(C) Gravimetrically, by separation with large excess of iron salts and ammonia. Place the clean weighed copper drillings in a beaker, and dissolve on a steam plate in strong nitric acid (sp. gr. 1.42).

For refined copper, containing less than 0.03 per cent arsenic, we take 50 grms. of copper, and treat with 210 cc. of acid, in a No. 7 beaker, but in the case of more impure material, it is sufficient to take 25 grms., or less, and treat in a No. 5 beaker (capacity 500 cc.) with 110 cc. of acid.

Dilute with water until the beaker is nearly half full, and add, to each assay, a solution of 2 grms. of chemically pure crystallised ferrous sulphate, which has been oxidised in a small beaker by heating with excess of nitric acid.

Heat nearly to boiling, and add strong ammonia until the iron is precipitated and the copper salts re-dissolved.

Fifty grms. of metal will require about 300 cc. of ammonia. Heat to boiling, settle one-half hour on steam plate, and filter quickly through a 15 cm. washed filter, supported by a platinum cone with coarse perforations. It is necessary to keep the solutions warm to prevent crystallisation, and the blue colour is washed out of the filter with water made slightly alkaline ($\text{rNH}_4\text{OH} : 10\text{H}_2\text{O}$).

If the bismuth is to be determined with antimony, add 2 grms. of ammonium carbonate and 5 cc. of saturated sodium phosphate solution to the solution as soon as the iron is precipitated as hydrate.

When the sample contains less than 0.100 per cent arsenic + antimony, the filtrate is passed through a second filter, to recover any traces of iron mechanically lost in the first washing.

If the copper is more impure than the above limit, make the blue filtrate acid with nitric acid, add 0.500 gm. of the oxidised ferrous sulphate, and precipitate and filter again to clear the solution.

Re-dissolve the large precipitate in dilute sulphuric acid, treat the filter-paper with a little ammonia, precipitate again, and pass through the same filter. If a second iron precipitation was made, dissolve this small amount of iron, add it to the blue filtrate from the last treatment of the major precipitate, and add excess of ammonia, and filter on a small filter.

Combine the two precipitates, dissolving them in hot dilute sulphuric acid, containing 5 per cent by volume of hydrochloric acid, and throw down the arsenic, &c., with

the last traces of copper, by fifteen minutes' cold treatment with a stream of hydrogen sulphide.

Allow to stand until granular and well settled, then, before night, charge again with the gas, and allow to settle over night.

In the morning, pass gas again until the solution smells strongly, and filter on a 7 cm. filter, then wash the beaker and tube by rubbing with bits of filter-paper. Transfer paper and contents to a small No. 6 beaker.

By the double gas treatment before filtering, the arsenic is generally brought down with the copper, instead of after it, but the filtrate should be charged with gas again and allowed to stand until settled, and the operation repeated until precipitation is complete. We dissolve the sulphides of arsenic and antimony with traces of tin by hot digestion with sodium sulphide, using as little as possible, and washing, by stirring and pressure, with slightly alkaline hydrogen sulphide water. Heat and filter again if any copper goes through, add 0.2 gm. solid sodium hydrate, or potassium hydrate, and evaporate to dryness on the steam plate, then treat the residue with about 20 cc. of the strongest fuming nitric acid, and digest until the sulphur is dissolved.

The method of oxidation of sulphides with hot hydrochloric acid and potassium chlorate sometimes involves a loss of arsenic.

Remove the cover from the beaker if the arsenic is to be subsequently weighed, and evaporate to dryness again.

If the arsenic is to be separated from other elements, the following method used in Montana is found to be superior to distillation.

Dissolve the dry residue in 25 to 50 cc. of hydrochloric acid, 2 parts of acid (sp. gr. 1.2) and 1 of water, adding a small crystal of tartaric acid. Precipitate the arsenic from a cold solution with hydrogen sulphide, allow to settle for a short time, and filter on an asbestos felt, and wash with acid of the same strength.

As soon as the filtrate is washed out and sulphide wiped from the beaker with a little asbestos, the filtrate can be removed and the acid removed from the felt with some H_2S water.

Test the acid solution again, and if no more arsenic appears throw down the antimony and traces of tin and copper with H_2S gas.

Selenium or tellurium, if present in sufficient quantity to interfere, may be removed by reducing the HCl solution with sodium sulphite or SO_2 gas before the H_2S treatment.

It has been observed that distilled water, unless condensed in iron or glass, as also the ammonia and HCl , generally shows a trace of tin, and a blank test of the acids reveals a trace of arsenic, but rarely antimony. The felt, with the sulphides, is placed in a small beaker, the sulphur dissolved by digestion on the steam plate with red fuming nitric acid, the solution diluted with one and one-half parts of water, the asbestos filtered out, and the solution evaporated to dryness on the steam plate, with 0.1 to 0.5 gm. of sodium nitrate, according to the amount of arsenic present, if the latter is to be weighed as magnesium pyroarsenate.

Dissolve the residue in 5 cc. of cold water, with the addition of 10 drops of HCl and 0.1 gm. of tartaric acid.

Filter through a 2½ cm. filter into a 25 cc. beaker, unless the arsenic is known to be over 0.05 gm., and wash with as little water as possible from a fine jet. Make slightly alkaline with ammonia, when the liquid should be clear and not have a volume of more than 11 cc.

Add 3 cc. of magnesia mixture, make up to 20 cc. with strong ammonia, and stir five minutes. If the arsenic is excessive, increase the precipitant, and dilute with ammonia so that the total volume shall be 25 to 30 cc., of which one-third is free ammonia water.

Allow to stand over night in a cool place, filter on a 2½ or 3 cm. filter, aiding the transfer of the arsenic by the filtrate.

Wash with a fine jet of ammonia (1 to 3 of water) until

free from chlorine, dry in an oven, remove the salt to a glazed paper, and place the filter in a porcelain crucible.

Add a few drops of acid ammonium nitrate solution (saturated), char carefully, and repeat treatment until the paper is consumed without a perceptible odour of arsenic.

Transfer the remainder of the precipitate, and ignite at a full red heat over the Bunsen burner to a constant weight. The Mg mixture, Fresenius's formula, is as follows:—One part of magnesium sulphate crystals, 4 parts of ammonium chloride, 8 parts of water, and 4 parts of concentrated ammonia (sp. gr. 0.90). The Mg should be free from lime, and the mixture should not be used after it has attacked the bottle and dissolved glass from its interior.

Copper Free from Antimony.

(D) Dr. Hampe, the German pioneer in accurate copper analysis, invented the method involving the reduction of the solution of copper by sulphurous acid gas with the removal of selenium and tellurium, and the subsequent precipitation of the copper as the white sulphocyanate. Dr. H. F. Keller has given a good account of this familiar but somewhat tedious method, and the reader is referred to his paper for details (*Journ. Am. Chem. Soc.*, 1894, xvi., 784).

Lake Superior metal, not electrolysed, rarely contains antimony, hence it is not necessary to make the separation in (2:1) HCl if water free from tin is used or the arsenic is to be titrated instead of weighed.

To be continued.)

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 24, June 12, 1911.

2.6. Dibenzoyl-2.6-dimethylheptane and $\alpha\alpha'$ -Tetramethylpimelic Acid.—A. Haller and Edouard Bauer.—When trimethylene dibromide acts on sodium isopropylphenyl ketone in toluene, 2.6-dibenzoyl-2.6-dimethylheptane is obtained. Sodamide splits it up into benzene and the diamide of $\alpha\alpha'$ -tetramethylpimelic acid. The saponification of this amide by Bouveault's method gives tetramethylpimelic acid. When the chlorobromide of trimethylene acts on sodium isopropylphenyl ketone the chlorine derivative of 2.2-benzoylmethyl-5-pentane is obtained.

Ionising Radiation Emitted by Radium C.—Louis Wertenstein.—The study of the active deposit of radium (RaB and RaC) by Briggs's method shows that RaC emits a comparatively intense ionising radiation, the penetrating power of which is comparable with that of the radio-active particles. It is only slightly deviable by a magnetic field.

Decomposition of Water by Metals.—Miroslaw Kernbaum.—When water is decomposed by zinc dust some hydrogen peroxide is always produced, but only in presence of air or free oxygen. The reaction is represented by the equation $\text{Zn} + \text{H}_2\text{O} + \text{O}_2 = \text{Zn}(\text{OH})_2 + \text{H}_2\text{O}_2 + \text{H}_2$. The mechanism of the decomposition of water in the cold by all metals is the same. The author has previously observed that water is sometimes decomposed abnormally according to the equation $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$, the reaction being induced by various radiations, whereas the normal decomposition is $2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$, effected by heat or the electric current. From the results of the present experiments, however, it appears as if these two reactions occur consecutively.

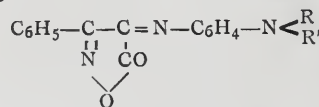
Catalytic Preparation of Ether Salts of Acids of the Formic Acid Series.—J. B. Senderens and J. Aboulenc.—When acetic acid and ethyl alcohol are distilled together in presence of aluminium sulphate, potassium bisulphate or sulphuric acid ether salt is obtained.

The best catalyser is sulphuric acid in the proportion of 1 or 2 per cent of the volume of alcohol and acid. In the case of ethyl acetate potassium bisulphate is a better catalyser than aluminium sulphate, while the latter is more effectual for other ether salts.

Action of Isobutylamine and Di-isobutylamine on α -Bromobutyric Acid.—Jean Nivière.—The action of isobutylamine on α -bromobutyric acid gives α -isobutylamino butyric acid. The acid forms lamellæ, which under the action of heat sublime without fusing, giving up ammoniacal vapours. It is soluble in water and alcohol, and insoluble in ether. Di-isobutylamine reacts with α -bromobutyric acid to give only α -oxybutyric acid.

Hydrogenation of Limonene.—G. Vavon.—The catalytic hydrogenation of limonene in presence of platinum black gives first the dihydride $\text{C}_{10}\text{H}_{18}$, and this subsequently absorbs two atoms of hydrogen to give the tetrahydride. The author has determined the physical constants of the dihydride, and has obtained from it the dibromo-derivative $\text{C}_{10}\text{H}_{18}\text{Br}_2$ by the action of bromine and the nitrosochloride $\text{C}_{10}\text{H}_{18}\text{NOCl}$ by the action of amylnitrite and hydrochloric acid.

Azomethines Derived from Phenylisoxazolone.—André Meyer.—The condensation of phenylisoxazolone with the equimolecular quantity of aromatic paranitrosamine can be effected by heat without any catalyser, a quantitative yield of azomethines of the formula—



being obtained. The nitrosopyrazols react similarly with phenylisoxazolone. All these products exhibit interesting colouring properties.

MISCELLANEOUS.

Technical Museum in Vienna.—The Technical Museum in Vienna has published a circular stating that, in commemoration of the sixtieth anniversary of Emperor Francis Joseph's reign, Austrian manufacturers, with the assistance of the State and the City of Vienna, have initiated a new Museum. The foundation stone was laid on June 20th, 1909, and the building, which covers an area of over 20,000 square yards, and which is situated opposite the palace of Schoenbrunn, is now nearing completion, and will be a lasting monument to the monarch. This Technical Museum is to demonstrate the development of industries and crafts in historical succession, also to do justice to the technical achievements of the present day, and to promote progress in this line by periodical exhibitions. It is to be a public educational centre, spreading a knowledge of the scientific foundations and the national economic aims of technical pursuits. A considerable stock of objects has already been secured, as several large and valuable State collections, till now dispersed, are shortly to be brought together there. But many links in the chain of technical development are still missing. Therefore technical scientists, manufacturers, and craftsmen of all countries are invited to cooperate in this great task and to assist the Museum in procuring and selecting suitable objects. Everything pertaining to technical labour is acceptable, principally tools, machines, apparatus, models, materials, methods of working, finished articles, as well as plans, designs, books, illustrations, and manuscripts. The Austrian Government has placed at their disposal the spacious halls of the Rotunda ("Prater") for the present storing and sifting of arriving donations. The names of donors will be perpetuated by inscription on the gifts and in a memorial book. Further particulars can be obtained from the office of the Technical Museum, Vienna I., Ebdorferstrasse 6.

THE CHEMICAL NEWS.

Vol. CIV., No. 2700.

SPECTROSCOPIC PROOF OF THE REPULSION BY THE SUN OF GASEOUS MOLECULES IN THE TAIL OF HALLEY'S COMET.

By PERCIVAL LOWELL.

1. THE return of Halley's comet has been noteworthy chiefly for the possibility of employing upon it modern methods of instrumental research. Since its last previous apparition have been devised those two great engines of astronomic exploration, spectroscopy and celestial photography. The former has afforded us our first direct knowledge of the substances composing comets, while the latter has given us a means of easy and rapid registration of the visitant's appearance. This is especially valuable in the case of a body as vast and vague as a comet, free-hand drawing of which is peculiarly liable to distortion.

During the last return of Halley's comet that body was subjected at Flagstaff to investigation by both instruments simultaneously. One result of this was the detection that gaseous molecules—in contradistinction to minute solid particles merely—are directly repelled by a force emanating from the sun, presumably the pressure of light. Previously this had been held impossible. Schwarzschild had, as he thought, demonstrated mathematically in an able paper that molecules of gas were too small to be thus affected by the forces concerned, and Arrhenius had adopted his deduction and published it as a fact in his "Worlds in the Making." That the bodies themselves would so soon refute this would not have been deemed probable, and invests the detection with the more immediate interest. Incidentally we may remark that Schwarzschild had since given up his original opinion.

2. That the tail of a comet is due to repellent force exerted by the sun is apparent from the direction the tail takes. For that direction agrees with what would be shown by particles leaving the nucleus and travelling in hyperbolic orbits away from the sun, the sun being in the full or the empty focus according to the speed of recession.

Although the general fact is thus evident, to measure the recession directly is to obtain both an observational proof of it and also something approaching an exact value of the velocity at a given time and place. Accordingly I determined to do this in the case of Halley's comet at its recent apparition. At my disposal were the two hundred photographs taken of it at the Lowell Observatory between April 18 and June 6. To obtain trustworthy results the photographs to be compared must not be separated by too long an interval, since with time a general commingling of the various particles takes place which not only renders particular decipherment of different outbursts impossible, but entirely alters the actual speeds. In the case of Halley's comet this difficulty was enhanced by the unusual uniformity of the tail. Irregularities, bunches, or knots were rare; the tail presenting, as a rule, a remarkably orderly deportment, dishearteningly same. Among the many plates, however, I was able to select a pair taken seriatim capable of recognition and measurement. Some of these handles to investigation were in the nature of bunches of matter, some of abrupt changes in its direction looking like promontories along the general line of the tail. I chose four of the more salient excrescences, and selecting identical features of them in the two negatives measured their respective distances from the nucleus on the two plates. The first plate was exposed from 9 hrs. 23 min. to 9 hrs. 53 min., and the second from 10 hrs. 0 min. to 10 hrs. 53 mins., so that the one followed directly on the other.

When the angular amounts of the changes in place of the several knots were corrected for differential refraction and then reduced to speeds, account being taken of the distance of the comet from the earth and of the inclination to the line of sight of the respective positions along the tail, the results came out as follows:—

Tail of Halley's Comet.

	Angular distance from the nucleus to the point measured in the tail.	Velocity of the point of the tail away from the nucleus.
Knot 1	1° 28'	13.6 miles a second
Knot 2	3° 12'	17.2 "
Knot 3	4° 36'	19.7 "
Knot 4	6° 15'	29.7 "

From these measurements the fact emerges unmistakably that a repulsive force directed away from the sun acted upon the particles on the tail.

3. While the series of direct photographs was being taken two series of spectrograms were being carried on by Dr. Slipher, one with an objective prism, the other set through a slit. The objective prism ones recorded simultaneously the spectrum of the nucleus and head, together with that of the tail out to about 11° from the nucleus. One of them was got on May 23 at the same time as the photographs measured; while others were obtained on dates before and after. Of the direct information afforded by these spectrograms of the constitution of the comet an account is given in the extensive monograph on the comet published by the Lowell Observatory.

4. But a third result was obtained by the unwitting collaboration of the spectrograms and the photographs. While the photographs were giving their pictures of the tail, the objective prism spectrograms were doing the like, with this difference, that they recorded in a row pictures of it in the several colours of the spectrum, sifting out into a band those made by each separate wave-length of light. They thus made it possible to tell to what wave-lengths the visible appearances were due. For it became evident at once from the spectrograms that all wave-lengths were not equally concerned. On the contrary, there were in the spectral image several distinct tails with spectral gaps between. By an analysis of the wave-lengths yielding pictures of the tail was thus offered a diagnosis of the substances composing it. In this way it appeared that CO₂, carbon monoxide, was the chief constituent of the tail; CH₄, marsh gas, another; CN, cyanogen, a third component; and minute solid particles, giving a more or less continuous spectrum, a fourth.

That not one but a series of spectrograms was taken was important. It not only gave us a constitutional history of the tail but it showed the necessity of simultaneity in photographic and spectrographic observations for comparative purposes. For the series demonstrated that the constituents of the tail varied markedly from one period to another. Thus from April 29, 1910, to May 7 the spectrum of the tail was almost wholly emissive. On May 11 it had changed to one nearly continuous, while on May 23 it had become largely emissive again, and grew more so as time went on.

By comparing the photographic with the spectrographic series of representations of the tail a striking fact came to light. To appreciate this another point must be taken into account. In order to compare properly a photograph and a spectrogram, both should be made on the same brand of plate. No plate reproduces all parts of the spectrum with equal intensity. One kind of plate will emphasise certain rays and depreciate others; the next will reverse the estimation. Great error will then be introduced unless the plates be identical.

Now the photographs measured were taken with a Brashear 5-in. doublet, an excellent lens, on a Lumière Σ plate. The rays registered by this plate extend from 3500 in the violet to 5160 in the green, where the sensitiveness ceases. Indeed the effect would have stopped

sooner had it not been for the hydrocarbon emission at this point. The light, therefore, of the photograph would be exactly differentiated into its constituents by a spectrogram taken on a Lumière Σ plate. The only difference between the two would be due to the absorption of the objective prism, an absorption relatively greater for the violet than for the blue or green. This would work as much on one kind of light as on another of the same refrangibility, and as the two different kinds we are considering, the emission and the continuous spectrum, are about equally spaced in the region of the violet, the correction needed on this account is small. We may, then, directly gauge the character of the photograph's light by that of the objective prism spectrogram taken on the Σ plate.

This we now proceed to do. On the exact date of the photograph no Σ plate was used with the two objective prisms, though we have objective prism spectrograms on Cramer Iso. Instantaneous on May 23, 25, 26, 28, and 29. The nearest plate to the date in question was on May 29. Of this the best estimate gives for the constituents of the light of the tail at a distance of 3° to 6° from the head:—

80 per cent of emission bands of carbon monoxide,
20 per cent continuous spectrum,

the hydrocarbon emission being, at this distance from the head too feeble to show.

Comparing now the spectrograms taken with a Voigtlander lens and a Cramer Iso. Inst. plate on May 23, 25, 26, 28, and 29 we find that the ratio of the two kinds of light varied in the direction of relatively greater emission from the former to the latter date. On May 23 itself the plates are affected by moonlight, so that a direct comparison of the relative ratios is too difficult to be made a basis of direct comparison, but that of May 28 gives for the ratios in the tail 3° from the head:—

70 per cent emission of carbon monoxide,
5 per cent emission of hydrocarbons,
25 per cent continuous spectrum.

Putting these facts together we shall not be far out of the way in stating the ratio on May 23 of the emissive and continuous spectrum of the tail at a distance of from 3° to 6° from the head for the Σ plate as—

70 per cent emission spectrum, CO and CH_4 ,
30 per cent continuous spectrum.

We have then this interesting conclusion:—That the knots which showed the action of a repulsive force exerted from the sun were chiefly composed, not of solid particles, but of *molecules of gases*.

5. To clinch this deduction I next turned to comet Morehouse. Catechised in this connection it not only corroborated the fact but emphasised it. Before the time of measuring the velocities in the tail of Halley's comet I had done the like for comet Morehouse, the knotted character of its tail offering promising inducement. I was not aware that MM. Quenisset and Baldet, in France, and Prof. J. A. Miller, of Swarthmore, Pa., had measured photographs of this comet in this manner previously and detected the same accelerated motion away from the head which my own later measures showed. My measures have also revealed why certain previous observers, such as Barnard at Yerkes and Campbell at the Lick, had failed to find such evidence.

Of comet Morehouse this observatory possesses about sixty negatives taken by Mr. E. C. Slipper. Among them are many pairs, the one plate following the other on the same evening. From the assortment thus offered I have selected two sets for measurement, the one a pair taken on October 31, 1908, at 8 h. o m. $\pm$ to 8 h. 42 m. $\pm$ M.S.T., and from 9 h. 14 m. $\pm$ to 10 h. 8 m. $\pm$ respectively; and the other a triplet on November 16, 1908, No. 1 being taken at 6 h. 25 m. to 7 h. 13 m.; No. 2 at 7 h. 24 m. to 7 h. 50 m.; No. 3 at 8 h. o m. to 8 h. 32 m. respectively. I chose

four knots on one and five on the other, with the following results:—

Tail of Comet Morehouse, October 31.

	Plate I., distance knot from head.	Plate II., distance knot from head.	Difference I. and II.
Knot 1 ..	22'8"	24'4"	1'6"
Knot 2 ..	72'7"	76'2"	3'5"
Knot 3 ..	95'5"	99'4"	3'9"
Knot 4 ..	128'4"	134'6"	6'2"

Tail of Comet Morehouse, November 16.

	Plate I.	Plate II.	Plate III.	Diff. I.—II.	Diff. II.—III.
Knot 1	48'7"	49'9"	51'4"	1'2"	1'5"
Knot 2	63'4"	65'4"	66'9"	2'0"	1'5"
Knot 3	79'7"	81'6"	83'5"	1'9"	1'9"
Knot 4	87'8"	89'3"	90'9"	1'5"	1'6"
Knot 5	211'1"	215'0"	217'7"	3'9"	2'7"

6. It will at once be seen that both sets of plates show accelerated velocity in the particles of the tail away from the head as the distance from the head increases. In the first set the acceleration is fairly uniform, while in the latter the velocity does not increase until the distance out has become considerable. This affords the reason why some observers have failed to detect the motion. It is at times and in certain places masked. For this the following explanation may be offered:—In the neighbourhood of the head the several emissions are violently contorted, as a mere inspection of the photographs show, and in consequence must be subject to collision with other portions of the tail. Possibly they encountered here matter in space which speaks unmistakably of motion other than that due solely to repulsive force. If now an observer chanced to make his measures at this inopportune moment he would naturally conclude that no repulsion existed, while in truth another motion was temporarily obstructing it.

7. Lastly, the spectrograms and spectroscopic observations of Frost and Pankhurst, de la Baum Pluvinel, and Baldet agree in showing the light of the tail of Morehouse's comet to have been due practically wholly to emission; in other words, to glowing gas. Here, then, we have not only corroboration of the fact, brought forward from study of Halley's comet, to wit, that molecules of a gas are repelled by the sun, but, from the light of the tail being composed solely of gaseous molecules, any supposition that they were not the cause of the visible effect is entirely excluded.

We reach, then, this interesting conclusion:—That molecules of gas not only may be but demonstrated are repelled by the action of the sun, and that though we have reason to suppose that minute solid particles may be similarly impressed, it is of the former, not the latter, that we have direct proof at present.—*Proceedings of the American Philosophical Society*, l., No. 199.

ON THE BEHAVIOUR OF FUSED SILICA AT HIGH TEMPERATURES.*

By A. BLACKIE, B.A., Assistant at the National Physical Laboratory.

(Concluded from p. 79).

3. *Relative Coefficients of Expansion of the Opaque and Transparent Varieties of Fused Silica.*

No investigators as yet appear to have made experiments on the coefficient of expansion of the opaque or translucent variety of fused silica, although several have made lengthy experiments on that of the transparent material. These experiments have been summarised in a convenient form in a paper by Dr. Kaye (*Phil. Mag.*, Oct., 1910), who shows that the best results are now in very good agreement over the temperature range— 200° to $+1400^\circ$ C., and that the coefficient, although very small, may now be taken as known with considerable accuracy.

* A paper read before the Faraday Society, May 23,

To determine the properties of the opaque variety approximately it is therefore only necessary to compare it with the transparent material, a far easier matter than making an absolute measurement. An apparatus for measuring the difference of expansion can be comparatively simple, and even if errors of 10 per cent in this difference were made, they are negligible if the difference be small compared with the absolute coefficient of expansion.

The method adopted for making the necessary measurements employed a well-known optical device for obtaining high magnification of small changes of length. Two parallel rods or tubes of the material are fused together at one end. Their free ends are furnished with parallel plane surfaces between which a needle rolls, and which are kept in contact with the latter by means of a small C spring. To the needle is fixed a small mirror on which falls a beam of light. From the motion of the reflected beam the relative movement of the free ends can be calculated. By using a small needle and a long beam of light a very great magnification can be obtained, and in

the temperature distribution at different heights was carried out at several steady temperatures. The mean temperature of the tubes corresponding to a reading of the fixed couple was thus deduced.

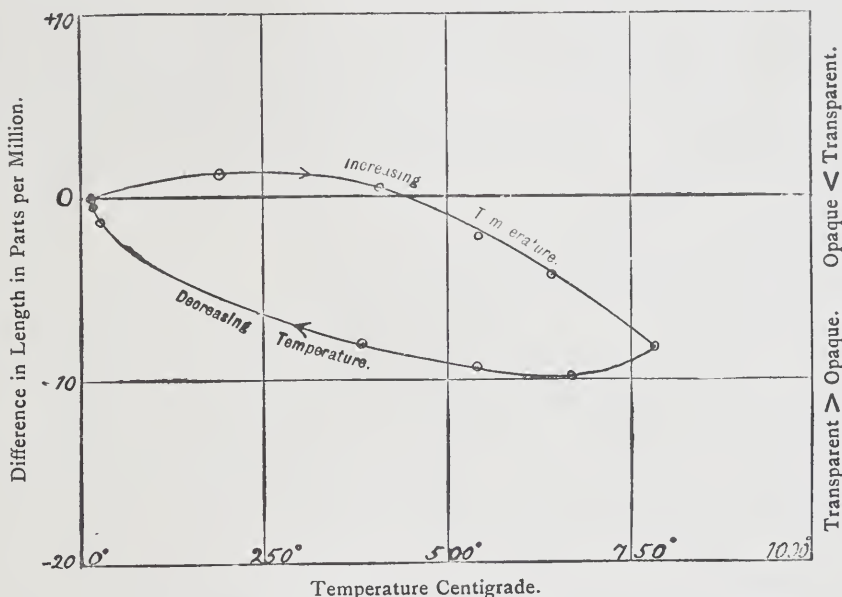
Experiments.

§ 3. In all, three independent groups of experiments were made in connection with this research, each involving a separately prepared apparatus.

The first set of experiments were merely qualitative, and were made with a very simple apparatus.

The second group of experiments was made with an opaque apparatus which consisted of an outer tube of silica, and a rod of transparent silica 24.3 cm. long. This was heated and cooled several times, and a number of measurements were made with this apparatus.

The third group of experiments was made with a similar apparatus which consists of a specially straight outer tube of opaque silica, and an inner tube of transparent material



RELATIVE EXPANSION OF OPAQUE AND TRANSPARENT SILICA. (Typical Graph).

the apparatus actually used in these experiments a difference in the lengths of the tubes of one part in ten million can be detected. The only source of any serious inaccuracy likely to arise is from the possible slipping of the needle, though it is hoped that in these experiments this has been almost eliminated. (It was found that by very slightly etching the needle used in picric acid, slipping can be almost entirely prevented). The heating of the tubes was carried out by means of a vertical nickel-wound electric furnace which could be lowered over the silica tubes without disturbing their adjustment, suitable arrangements being made for checking convection currents at the mouth of the furnace. Where the tubes emerge from the furnace there is bound to be a considerable temperature gradient, and any effects which this might have had were compensated for by making the inner tube composite. The upper portion, which is entirely inside the furnace, consists of transparent material, while the lower portion which passes through the furnace mouth-piece is made of the same material as the outer tube. The temperature of the furnace was measured by means of a single thermo-couple always kept at a fixed position. This, of course, only gives the temperature at that point in the furnace, and as this varies somewhat at different levels an exploration of

30 cm. long, both of which were supplied by the Thermal Syndicate for this purpose.

This was the apparatus with which most of the experiments were made.

Results.

§ 4. Both groups of experiments lead to the same main conclusions, which are as follows:—

(1) That the differences between the coefficients of expansion of transparent silica and either the "coarse" or "satin-like" material are very small.

(2) That in all cases the opaque materials have a slightly greater expansion than the transparent up to about 500° C., and that above that temperature the transparent silica expands most.

(3) That in both groups of experiments the expansion of one or both materials lags behind the temperature.

The transparent silica has the greater lag in experiments carried to the higher temperature (above 500° C.), but in one experiment where the highest temperature was only 360° the reverse was found to be the case.

(4) That on re-cooling to atmospheric temperature the lengths are usually not quite the same as before heating, and that a slow change of length takes place in one or both materials for some time afterwards, though from

practical points of view this is too small to be of any moment. In view of these slight variations it was decided to count all expansions from the zero determined previous to each experiment.

A typical curve obtained during heating and cooling is shown. The temperature was steady for fifteen minutes during each observation shown in the graph.

Discussion of Results.

§ 5. (1) Taking the first of these points the *greatest* difference in length noted during the period of heating for a rise in temperature of 800°C . is 25 parts in a million of the total length, or, in other words, 25 microns per metre. During cooling, owing to the difference in the lag of the two materials, this becomes 30 microns per metre in an extreme case. In most cases, however, the differences are smaller, as shown in the graph. The differences are, in fact, very much less than the differences between the absolute expansions of transparent silica as determined by any two observers up to date.

To view the matter in another light the difference of expansion at 500°C ., a temperature at which platinum can be sealed to lead glass, is about 150 parts per million. This may be compared with the maximum of 25 or 30 parts per million found between the two tubes of silica at 800°C .

(2) Taking the second point, it is obvious from the graph that for the first 400° or 500° the opaque silica expands most, and that then the position is reversed. From the practical point of view this hardly requires any comment when the smallness of the effects is remembered.

Also it must be kept in mind that the fact that most of the graphs like that shown cross the zero line at about 500°C . does not imply any actual contraction of either tube, but only that the expansions of one or both cannot be expressed by a linear formula.

(3) The fact that the expansion of one or both types lags behind the temperature is not in itself astonishing, having been noticed in many substances, especially those of composite nature. Its actual magnitude cannot be determined from these experiments, all that is indicated being the difference of lag of the two tubes. This lag has also been noticed by Callendar.

(4) Closely connected with the lag is the slow relative change of length that appears to take place after reaching atmospheric temperature. This also is an effect found in a large number of substances, such as glass, brass, invar, &c.

In some experiments made in the metrology department of the National Physical Laboratory a relatively large permanent change of length was found in a transparent rod after heating for a few hours to 800°C ., and a smaller change in an opaque rod after heating to 400°C .

In both cases the rod became shorter. From the practical standpoint the changes were negligible, but were of importance from the point of view of the use of fused quartz as a material for standards of length. Callendar appears, on the contrary, to have found permanent elongations after heating to 1000°C ., and without further experience of a larger range of samples it is difficult to express a definite opinion as to the permanent changes of length caused by thermal treatment.

It was found in the present series of experiments that the rate of change of length after cooling of the two materials was different, and a marked motion of the needle took place for several days. The experiments also showed clearly that the difference in this rate of change is much greater when the maximum temperature reached was above 500°C . than when below it. Dr. Kaye summarises the present position with regard to lag in the paper already mentioned.

It may be taken that as far as the coefficient of expansion is concerned the differences between the two classes of silica are for practical purposes negligible, though from the theoretical standpoint and that of the more exact

work required in connection with standards of length they may be of more importance and worthy of further study.

In conclusion, I wish to thank the Director, Dr. Harker, and other members of the staff of the National Physical Laboratory for their kindly interest, advice, and help during the course of the investigations, and to acknowledge the ready manner in which the Thermal Syndicate supplied suitable materials for the research.

A REVISION OF THE ATOMIC WEIGHT OF IRON.*

THIRD PAPER.—THE ANALYSIS OF FERROUS BROMIDE.

By GREGORY PAUL BAXTER,
THORBERGUR THORVALDSON, and VICTOR COBB.

(Concluded from p. 81).

5. Balance and Weighing.

ALL the weighings were performed in a Troemner balance No. 10, easily sensitive to 0.02 mgrm. The gold-plated brass weights were standardised from time to time by the method described by Richards (*Journ. Am. Chem. Soc.*, 1900, xxii., 144). No changes of more than a few hundredths of a milligram were found, however. Variations in the weights of containing vessels owing to changing atmospheric conditions were avoided by using counterpoises of the same material and as nearly as possible of the same shape and volume. The following vacuum corrections were applied:—

	Specific gravity.	Vacuum correction.
Weights	8.3 (a)	—
Silver	10.49 (b)	− 0.000031
Silver bromide ..	6.473 (c)	+ 0.000041
Ferrous bromide ..	4.636 (d)	+ 0.000114

(a) Baxter, *Proc. Amer. Acad.*, 1906, xlii., 209; *Journ. Am. Chem. Soc.*, xxviii., 1321.

(b) Richards and Wells, *Pub. Car. Inst.*, 1905, xxviii., 11; *Journ. Am. Chem. Soc.*, xxvii., 466.

(c) Baxter and Hines, *Am. Chem. Journ.*, 1904, xxxi., 224.

(d) Baxter, *Proc. Amer. Acad.*, 1903, xxxix., 251.

In the accompanying tables are given the results of all the analyses completed, except three which met with known mishaps. The analytical work was performed wholly by Mr. Thorvaldson.

In seeking to discover the most probable value for the atomic weight of iron indicated by the foregoing data, it is only fair to bear in mind that the first experiments of a series are almost invariably influenced by incidental experimental errors which are largely eliminated in later experiments. Furthermore, the first three samples of ferrous bromide to be analysed were fused in hydrobromic acid prepared from bromine and red phosphorus, and hence may have contained traces of phosphorus, while a hard glass tube was used in the fusion of the next four samples. We have therefore collected in the two preliminary series the first seven analyses, made in the summer and fall of 1909. The two final series were completed during the winter of 1909-10 after a very considerable intermission, and are, in our opinion, much more satisfactory and less subject to avoidable errors.

The averages of the two final series agree perfectly, showing that so far as the estimation of the bromine is concerned no serious constant error exists. This is further indicated in the following table, where the ratio of silver used and silver bromide obtained in the different pairs of analyses is recorded:—

* From the *Journal of the American Chemical Society*, xxxiii., No. 3.

Preliminary.		Ag : AgBr.
Analyses	1 and 19	0.574502
	2 and 20	0.574460
	5 and 21	0.574438
	6 and 22	0.574428
Average		0.574457
Final.		
	8 and 23	0.574461
	9 and 24	0.574451
	10 and 25	0.574432
	11 and 26	0.574471
	13 and 27	0.574444
	14 and 28	0.574471
	15 and 29	0.574439
	16 and 30	0.574440
	17 and 32	0.574448
	18 and 33	0.574464
Average		0.574452

The average ratio agrees with the value to be expected, 0.574453 (Baxter, *Proc. Amer. Acad.*, 1906, xlii., 210; *Journ. Am. Chem. Soc.*, xxviii., 1332).

The different samples of ferrous bromide appear to be exactly similar as far as can be told by the results of the analyses. The following table contains a comparison of the averages from the different samples in the final series.

Sample.	FeBr ₂ : 2Ag.	FeBr ₂ : 2AgBr.	Average.
A	55.837	55.843	55.840
B	55.837	55.835	55.836
C	55.839	55.838	55.839
Average	55.838	54.839	55.838

In the final series 60.64794 grms. of ferrous bromide combined with 60.67313 grms. of silver, whence the atomic weight of iron is 55.838, while 64.68065 grms. of ferrous bromide produced 112.64198 grms. of silver bromide, the amount to be expected if the atomic weight of iron is 55.838.

No matter how the results are treated, the outcome is the same. This method indicates a value for the atomic weight of iron of 55.838 if silver is taken as 107.88.

Certain possible constant errors needed to be discussed. In two analyses of ferrous bromide prepared from meteoric iron, described in a following paper on the atomic weight of meteoric iron, the oxidation of the ferrous bromide to the ferric state before the precipitation of the silver bromide was carried out with 98 instead of 99 per cent of the theoretical dichromate necessary. These two analyses yielded results very slightly lower than analyses with similar material in which 99 per cent of the theoretical dichromate was used, owing possibly to reduction of silver salts by the residual ferrous salt. The question naturally arises whether 99 per cent of dichromate is enough to prevent reduction of silver salts. In this connection it must be remembered that the ferrous salt was from the moment of solution undergoing continual oxidation, and that in reality less than 1 per cent remained unoxidised after the addition of the dichromate. As the solution was always allowed to stand several hours after the addition of the dichromate, before precipitation, this oxidation must have been very considerable. Secondly, the average ratio of silver used to silver bromide obtained has exactly the proper value, which indicates that the silver bromide contained no excess of silver. This point is substantiated by the appearance of the fused silver bromide, which, as has already been stated, was light yellow and transparent. Furthermore, the reducing effect of ferrous salts on silver salts diminishes with the concentration of both substances. For instance, while a 0.5 per cent acid solution of ferrous sulphate gave a precipitate of silver with an equal amount of a 0.06 per cent solution of silver nitrate on standing over night, the same ferrous solution gave no precipitate with a 0.03 per

cent solution of silver nitrate. Similarly a 0.1 per cent solution of ferrous sulphate gave no precipitate with even a 20 per cent solution of silver nitrate. Since in an analysis the concentration of silver nitrate used in precipitation was never over 1 per cent., while, if 1 per cent of the ferrous bromide was unoxidised, the concentration of the latter substance could never have been higher than 0.003 per cent, the possibility of reduction was certainly small.

Although one of us has already shown that it is possible to free ferrous bromide from ferric salt by heating in a current of nitrogen and hydrobromic acid gases to about 400° (Baxter, *Proc. Amer. Acad.*, 1903, xxxix., 246), the experiment for the detection of ferric salt was repeated with the fused ferrous bromide. The salt fused as described above was transferred to the weighing bottle in an atmosphere of nitrogen. The stopper of the weighing bottle was then removed and a freshly boiled and cooled slightly acid solution of ammonium thiocyanate was quickly poured into the bottle, completely filling the bottle. The bottle was again stoppered, and allowed to stand until the ferrous bromide was dissolved. Although the solution did not remain perfectly colourless, the colour of the ferric thiocyanate was not strong. By comparison with solutions of known amounts of ferric iron the quantity of ferric bromide was found to be less than 0.05 mgrm. So slight an amount of oxidation as this might well have occurred during the solution of the salt. At any rate it is obviously unnecessary to apply a correction of this magnitude.

The question of the neutrality of the ferrous bromide is difficult to settle, in particular because a basic precipitate is formed by oxidation as soon as the salt is dissolved in water. In many similar instances, however, where metallic bromides have been fused and allowed to solidify in hydrobromic acid gas, the salts have been found to be essentially neutral, hence it is fair to assume that this is the case with ferrous bromide also, especially since the concentration of the hydrobromic acid gas was never very high during the fusion. Furthermore, if the salt was not neutral, such variations in the method of heating and fusing as actually occurred would be expected to produce variations in the basicity or acidity of the salt. That such variations were inappreciable is indicated by the agreement of the different results. None of the specimens of fused ferrous bromide gave a perfectly clear solution, even when dissolved in water containing considerable acid. The insoluble substance consisted of a trace of black material, undoubtedly carbon, since it disappeared when collected on a filter and ignited, and a very small amount of a light coloured precipitate visible only under the most favourable conditions. The quantity of both kinds of material varied somewhat in different fusions, and in the most successful experiments the insoluble material was almost entirely absent. Variations in the manner and speed of heating the ferrous bromide seemed to have no perceptible effect on the quality of the fused material.

Finally, the attempt was made to determine the weight and composition of the residue. Acidified solutions of fused ferrous bromide were filtered through tiny filters, and the papers were thoroughly washed. The filtrates seemed perfectly clear. The filters were ignited, and the residues weighed in platinum crucibles. Since many salts of heavy metals are adsorbed from solution by filter-paper (Baxter and Hines, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1569; Baxter and Wilson, *Proc. Amer. Acad.*, 1907, xliii., 369; *Journ. Am. Chem. Soc.*, xxx., 191), blank experiments were carried out by filtering again the once filtered solutions. In four experiments the residues obtained from the original material weighed 0.30, 0.14, 0.15, and 0.12 mgrm., while three blank experiments yielded 0.13, 0.13, and 0.12 mgrm. of ignited residue. The four residues were boiled with aqua regia, and the solution was evaporated. The solution was found to contain a trace of iron, while a slight insoluble grey residue which appeared to be silica remained. Whatever the composition of the residue, its weight is insignificant. If the residue was silica, it may

ATOMIC WEIGHT OF IRON.

Ag = 107.88.

Br = 79.916.

Preliminary Series I.—FeBr₂ : 2Ag.

No. of analysis.	Sample of FeBr ₂ .	Weight of FeBr ₂ in vacuum. Grms.	Weight of Ag in vacuum. Grms.	Weight of Ag added or subtracted. Grm.	Corrected weight of Ag in vacuum. Grms.	Ratio, FeBr ₂ : 2Ag.	Atomic weight of iron.
1.	A	3.45339	3.45441	0.00040	3.45481	0.990589	55.840
2.	A	3.04933	3.05030	0.00025	3.05055	0.999600	55.841
3.	A	2.9007	2.9018	0.0001	2.9019	0.999586	55.839
4.	B	3.0873	3.0884	0.0001	3.0885	0.999611	55.844
5.	B	3.50278	3.50416	0.00010	3.50426	0.999577	55.837
6.	B	4.05239	4.05379	0.00025	4.05404	0.999593	55.840
7.	B	4.08516	4.08653	0.00030	4.08683	0.999593	55.840
Average						0.999593	55.840

Final Series I.—FeBr₂ : 2Ag.

8.	B	5.03555	5.03769	0.00005	5.03774	0.990565	55.834
9.	C ₂	6.06309	6.06557	0.00000	6.06557	0.999592	55.840
10.	C ₂	5.59258	5.59492	—0.00010	5.59482	0.999599	55.842
11.	C ₁	5.89767	5.90014	0.00000	5.90014	0.999581	55.838
12.	C ₁	5.48546	4.48732	0.00010	4.48742	0.999563	55.834
13.	B	5.41562	5.41794	0.00005	5.41799	0.999563	55.834
14.	A	6.50002	6.50272	0.00005	6.50277	0.999577	55.837
15.	C ₁	3.56564	3.56719	0.00000	3.56719	0.999565	55.834
16.	B	5.32434	5.32662	—0.00020	5.32642	0.999609	55.844
17.	C ₃	6.38845	6.39124	—0.00030	6.39094	0.999610	55.844
18.	C ₃	6.37952	6.38223	—0.00010	6.38213	0.999591	55.840
Total		60.64794			60.67313	0.999585	55.838
Average						0.999583	55.838

Preliminary Series II.—FeBr₂ : 2AgBr.

No. of analysis.	Sample of FeBr ₂ .	Weight of FeBr ₂ in vacuum. Grms.	Weight of AgBr in vacuum. Grms.	Loss on fusion. Grm.	Corrected weight of AgBr in vacuum. Grms.	Ratio, FeBr ₂ : 2AgBr.	Atomic weight of iron.
19.	A	3.45339	6.01412	0.00054	6.01358	0.574265	55.853
20.	A	3.04933	5.31057	0.00028	5.31029	0.574228	55.844
21.	B	3.50278	6.10048	0.00015	6.10033	0.574195	55.831
22.	B	4.05239	7.05799	0.00047	7.05752	0.574195	55.831
						0.574.221	55.840

Final Series II.—FeBr₂ : 2AgBr.

23.	B	5.03555	8.76960	0.00010	8.76950	0.574212	55.837
24.	C ₂	6.06309	10.55911	0.00022	10.55889	0.574216	55.839
25.	C ₂	5.59258	9.73988	0.00014	9.73974	0.574202	55.834
26.	C ₁	5.89767	10.27065	0.00008	10.27057	0.574230	55.844
27.	B	5.41562	9.43199	0.00028	9.43171	0.574193	55.830
28.	A	6.50002	11.31990	0.00032	11.31958	0.574227	55.843
29.	C ₁	3.56564	6.21000	0.00013	6.20987	0.574189	55.829
30.	B	5.32433	9.27263	0.00026	9.27237	0.574216	55.839
31.	C ₃	8.51818	14.83494	0.00026	14.83468	0.574207	55.836
32.	C ₃	6.38845	11.12550	0.00014	11.12536	0.574224	55.842
33.	C ₃	6.37952	11.11011	0.00040	11.10971	0.574229	55.844
Total		64.68065			112.64198	0.574214	55.838
Average						0.574213	55.838
Average of Final Series I. and II.							55.838

have been extracted from the quartz boat, which lost in weight at the rate of a few hundredths of a milligram. in each analysis.

The uncertainty introduced by the last three considerations is not large enough to affect the second decimal place in the atomic weight of iron. The rounded-off value 55.84 confirms the earlier work on ferrous bromide as closely as could be expected, while the greater purity of the ferrous bromide which we prepared gives greater probability to the result of this research than to that of the earlier one on the bromide. Since the bromide method of atomic weight investigation has been thoroughly tested

with numerous metallic bromides, the results of this investigation are entitled to greater weight than the earlier results from the analysis of ferric oxide. Until the opportunity is offered for investigating further the analysis of ferric oxide, it seems decidedly safer to employ the lower value for the atomic weight of iron yielded by the analysis of ferrous bromide.

In a following paper is described a continuation of this research by the determination of the atomic weight of meteoric iron.

We are particularly indebted to the Carnegie Institution of Washington for pecuniary assistance in carrying out this

investigation, and also the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

Following is a summary of the chief results of this investigation:—

1. A new method of preparing very pure ferrous bromide is described.

2. The analysis of this salt indicates that the atomic weight of iron is 55.838 referred to silver 107.880. If silver is assumed to have the atomic weight 107.870, iron becomes 55.833.

THE DETERMINATION OF ARSENIC AND ANTIMONY IN COPPER.*

By GEORGE L. HEATH.

(Concluded from p. 84).

New Volumetric and Electrolytic Method.

(E) This scheme of direct titration of an electrolyte is believed to be a new one, and will be found to permit much more rapid work with all classes of material containing little antimony, and can also be used with any copper by preparing the solution for electrolysis (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1120), separating the antimony and tin, if present, by methods previously published.

Such a method is adapted to routine control of impure material, and was developed for the assay of a large tonnage of Lake copper now produced, which runs high in arsenic, but has almost no antimony.

First. Modification for Copper with Less than 0.01 per cent of Arsenic without Antimony.—Dissolve the metal and separate the arsenic group as in method C, or perhaps D, but omit the final precipitation with hydrogen sulphide gas in (2:1) hydrochloric acid, as a trace of tin does not affect iodine in titration. In the rare case in which a trace of gold or platinum is present, the copper can be originally dissolved according to the method just devised by the writer, and which will be made the subject of a paper at once, on a "New Method for the Determination of Gold in Copper Bullion."

Weigh 1 assay ton of very fine drillings (taken with a $\frac{1}{4}$ in. drill) into a No. 4 casserole, add 25 to 30 grms. of chemically pure solid potassium bisulphate and 100 cc. of concentrated chemically pure sulphuric acid, cover, and boil carefully on a gauze, or plate, for ten minutes, when metal should be practically dissolved.

Decant acid without diluting much if possible, and boil any little residue with a little more acid mixture, then dilute, settle, and filter out gold and platinum. If selenium or tellurium is present, it can be reduced from the hydrochloric acid solution of the residue, obtained by evaporation of the first sodium sulphide solution of the arsenic group with fuming nitric acid. Treatment with sodium sulphite will effect reduction, or hydroxylamine as recommended by Dr. H. F. Keller.

The titration of an electrolyte gives a little too high results on arsenic, when the arsenic is less than 0.01 per cent, because of the presence of a minute trace of platinum which may be found in the electrolyte, and in much of the cathode copper, produced in the laboratory by the regular 5 gm. battery assay of refined copper.

Whether it has been found necessary to purify the arsenic sulphide from traces of antimony, Pt, and Se, or not, the residue from evaporation of the sulphide with fuming nitric acid and excess of soda is taken up with sulphuric acid, or better 25 cc. of strong sulphuric acid are added to the nitric acid solution of the arsenic as soon as the sulphur has disappeared. Instead of a little sodium nitrate which was recommended in the gravimetric method to hold the arsenic, we add 3 grms. of solid potassium bisulphate, free from chlorides. This is adapted from Low's method for ores ("Technical Methods of Ore

Analysis," q. v.). Heat rapidly on a hot plate until the sulphuric acid fumes for five minutes.

Cool, wash into a 300 cc. long-necked Kjeldahl flask of Jena glass, place in an inclined position on a lamp-stand over a small flame, boil off the water, fume five minutes again, and when the time is nearly up, flash the neck of the flask with a lamp flame, long enough to drive out any condensed liquid from the neck.

This double fuming process, and removal thereby of the last trace of nitric acid, is the *secret of success* with the process, as in the iodide method for titration of copper.

After the flask has cooled a little, add from a paper 0.5 gm. of solid tartaric acid, and, giving the flask a whirling motion occasionally, digest until the solution is colourless.

Allow to cool, wash into a No. 3 beaker, in which a little water has been placed, and fill the beaker about half full.

One advantage of this scheme is that a dozen digestions can be carried through as easily as one. Drop a small piece of litmus-paper into the beaker, add ammonia until the liquid is just alkaline, and bring back to the acid condition with dilute sulphuric acid, adding only one drop in excess.

Place the beakers in a large pan of water to cool, when they will be ready for titration with iodine.

This titration will be taken up after the description of the second electrolytic process.

(E) *Second Part. Electrolysis followed by Direct Reduction and Titration.*—This is the quickest of all methods for control work, and is accurate for any copper containing more than 0.01 per cent of arsenic and no more than a trace of antimony, but the latter if present would have to be removed unless it was permissible to neglect its influence.

If the metal contains less than 0.1 per cent of arsenic, we take two portions of 10 grms. of drillings and place them in the beakers used for the usual battery assay of copper, as described in the first paper.

Dissolve in a slight excess of strong nitric acid (sp. gr. 1.42), add 17 cc. of strong sulphuric acid, and evaporate to dryness.

A whole set may, of course, be started at once, and when dry, and the residue smells sweet, add 12 cc. of nitric acid and water sufficient to cover the electrode, which has the usual dimensions for copper assaying, about 100 sq. cm., counting both sides of the plate.

Pass a current of N. density - 1 ampère until colourless, then reduce to one-half an ampère; in short, perform the regular electrolytic assay for refined copper, just as described in the writer's first paper.

The small portion of liquid, removed for test, is washed into a little beaker, treated with a small crystal of potassium bisulphate, or sodium nitrate, and a few drops of sulphuric acid, and evaporated until the sulphur is gone, when it is transferred to the main solution now free from copper, which is treated with 3 grms. of the solid potassium bisulphate, and evaporated until the nitric acid is all driven off and the sulphuric acid has fumed strongly for five minutes.

The solution is then washed into a Kjeldahl flask and digested as already described. In very accurate analyses, the first copper cathode is re-dissolved in 40 cc. of "stock solution" as described in the paper on the electrolytic assay, and the copper again deposited and the second electrolyte boiled down with the first.

The "stock solution" mixture of dilute acids is not employed for the original solution of the drillings because it is necessary to oxidise all the arsenic to the condition of arsenic acid, or there appears to be some loss—due to the electric current.

If the metal has more than 0.1 per cent of arsenic, two 5-gm. assays are taken, using 15 cc. of sulphuric acid and a final addition of 10 cc. of nitric acid for each. If 0.2 per cent of arsenic is known to be present, each of the assays is boiled down, reduced, and titrated separately, or if the arsenic is less, they may be combined as one and boiled together.

* *Journal of Industrial and Engineering Chemistry*, iii., No. 2.

If the arsenic is between 0.01 per cent and 0.05 per cent, two 10-grm. assays are combined. The remarks on re-plating apply here.

A blank should be made with each new lot of acids, and digested. If selenium or tellurium is present, we dilute the dry residue of copper sulphate with water and reduce this element with excess of sodium sulphite free from chlorine, or with a rapid current of sulphurous acid gas at a temperature of 40° C., filter, and allow to settle before adding the nitric acid.

Notes on the titration of arsenious acid by iodine will follow.

If very rapid work is necessary, the solution can be electrolysed for removal of copper in the rotary device if water-cooled, but more traces of platinum are introduced into the electrolyte, and affect the iodine in titration.

In presence of antimony the electrolyte can be boiled down until the nitric acid is off, then diluted with one and one-half volumes of water, and strong hydrochloric acid added in amount equal to the total, and the arsenic separated by treatment of the cold liquid with excess of hydrogen sulphide.

Even with this modification this method is more rapid than the gravimetric or distillation, particularly as a number may be done at once, in conjunction with regular copper determinations.

A few words may be of interest in description of a large rotary device which is of great assistance in removing the copper from solutions of either 25 or 50 grms. of metal, in order that the electrolyte may be evaporated down to small bulk for the estimation of iron, zinc, nickel, cobalt, lead, &c., and, with an extra precaution to separate a trace of platinum, may be used to determine arsenic.

Dimensions:—Size of beaker, No. 4 and 5 low form, capacities 500 to 750 cc., permits the passage of 6 to 8 ampères, or more, of current through the coil and solution by water-cooling the space between beaker and cylinder.

The anode is a straight doubled wire, and the cathode is a large closed cylinder of foil 7.5 cm. in diameter, 11 cm. high, and perforated with holes 3 mm. in diameter, and spaced 1 cm. apart.

In the iron determination, 25 grms. of drillings are dissolved in 25 cc. nitric acid, 40 cc. sulphuric acid, and 100 cc. of water; 50 grms. would require 55 cc. of nitric acid, 80 cc. of sulphuric, and 250 cc. of water. Twenty grms. of copper for sulphur determination would be dissolved in 120 cc. of pure nitric acid and free acid removed before diluting with water. For arsenic test, 25 or 50 grms. of metal are dissolved in nitric acid, either 40 cc. or 80 cc. of sulphuric acid, and the nitric acid evaporated until the residue smells sweet, after which 25 or 50 cc. of nitric acid are added and residue dissolved, and electrolyte dissolved and electrolysed it has a chance to crystallise.

The use of the large rotary device is a success for the rapid separation of copper from most of the elements mentioned, but does not give as good results for arsenic as the electrolysis of 5 or 10 grms. by the slow method. It requires that a precipitation of the arsenic be made in (2 : 1) HCl to remove not only antimony but also a trace of platinum which is dissolved continuously from the anode by the nitrous acid and heavy current.

Notes on the Accurate Titration of Arsenious Acid by Iodine.—We have made many experiments to ascertain the proper conditions for the accurate titration of arsenious acid in either very small or large amount, and to eliminate slight errors which some chemical authorities have declared to be inherent in the titration.

In the first place we have found that sulphuric acid is a better medium than hydrochloric acid for final solution and neutralisation.

The blank tests for arsenic in the former acid or for the nitric acid used in the process are very small, but hydrochloric acid contains a variable trace of arsenic or element which distils and affects iodine.

The following are tests on two lots of chemically pure HCl from two makers:—

No.	Cc. acid taken.	Cc. of iodine.	Blank for end-point.	Cc. of iodine.	Arsenic found. Grm.
1.	100	0.22	0.08	0.14	0.00015
2.	100	0.32	0.08	0.24	0.00027

The HCl was neutralised with ammonia, using a piece of litmus-paper as indicator, cooled, made acid with one drop excess, and treated with 12 grms. of sodium bicarbonate; total volume, 300 cc. The soda should be free from iron.

We also find that the titration of traces of arsenic is rendered exact if three drops of a 10 per cent solution of potassium iodide are added. This supplies the conditions for a clear end-point with 2 cc. of a starch solution made up according to directions recently published (*Chem. Abs.*, 1910, iv., 2617). That authority directs that the starch shall be soaked twenty-four hours in very dilute HCl, then washed, dried, and heated three hours in a hot oven at 100° C. The end point thus obtained is a remarkably delicate blue, free from the muddy reddish tint given by ordinary starch indicator, and the blank for the amount to produce an end-point is only 0.04 cc. of iodine, of which 1 cc. = 0.001 gm. of arsenic.

Most of the printed methods direct that 2 to 4 grms. of sodium bicarbonate should be added to the slightly acidified solution before titration. In the titration of large quantities, or any unknown assay, we find it is an advantage to add a very much larger excess of pure soda, free from iron, as it insures a sufficient quantity of the ions present, which recent investigators have said to be necessary for the uniform action of the iodine and production of the iodide of starch. The use of the precautions mentioned, with cooling of the solution before the final addition of the bicarbonate of sodium, enables an operator to titrate a mgrm. of arsenic or 100 mgrms. as closely as one can precipitate it by magnesia and weigh it, and with more certainty for small amounts.

The iodine solution is made by dissolving 3.5 grms. of pure re-sublimed iodine, and 7 grms. potassium iodide in water, diluting to 1 litre, and allowing to stand in a brown bottle for at least twenty-four hours before use.

A 10 per cent solution of potassium iodide is also made, and 3 or 4 drops are added to every titration after the bicarbonate of soda.

Standardise with pure arsenious acid, of which 0.06 gm. portions are dissolved cold in a little water containing 1 gm., or less, of potassium hydrate, washed into a No. 3 beaker, diluted to nearly 300 cc., made slightly acid with sulphuric acid, using litmus-paper as an indicator.

Make slightly alkaline with ammonia, then faintly acid with 1 drop in excess of the acid, add the carbonate, and titrate rapidly until the end-point is nearly reached, employing 3 cc. of starch solution as the indicator and 3 drops of the 10 per cent solution of KI.

The beaker is allowed to stand on a white surface, and a fainter end-point is noted and taken with less than 5 mgrms. arsenic than when the quantity is large.

A table shows the agreement in the titration of varying amounts of arsenic with ordinary untreated starch indicator, which causes a higher blank test as shown. Results with the new starch are better, so much so that we now prefer to titrate arsenic in accurate analysis rather than to weigh it.

As taken.	Iodine total cc.	Blank test.	Net cc. of iodine.	Arsenic found. Grm.
0.0010	0.99	0.09	0.90	0.0010
0.0020	2.02	0.09	1.93	0.00214
0.00206	1.86	0.09	1.77	0.00196
0.0024	2.27	0.09	2.16	0.0024
0.0020	1.91	0.09	1.82	0.00202
0.00998	9.12	0.09	9.03	0.01002

A thermometer is attached to the burette, when standardising and during the regular work, and a correction is made to the burette readings for changes in the volume of the solution from that prevailing at the time of the standardisation.

THE ESTIMATION OF SILVER BY
ELECTRO-DEPOSITION FROM AN AMMONIACAL
SOLUTION OF THE OXALATE.*

By F. A. GOOCH and J. P. FEISER.

IN a recent paper from this laboratory an account is given of tests upon the efficiency of a silver anode in the fixation of chlorine derived from hydrochloric acid by electrolysis. It was found in these tests that when the silver anode was made by plating platinum gauze with silver in a solution of the double cyanide of silver and potassium, the silver deposit invariably included some of the potassium salt. To secure purity of the silver anode an ammoniacal solution of silver oxalate was substituted for the double cyanide solution in the plating process, for the reason that nothing

Sci., 1903, xv., 320), the double disc of gauze (Hillebrand, *Journ. Am. Chem. Soc.*, 1907, xxix., 450) and a gauze cone set point downward upon the axis of rotation. In the experiments of Table I., measured amounts of the silver nitrate solution (25 cc. or 50 cc.) were drawn from a burette into a small beaker and treated with ammonium oxalate to complete precipitation. The silver oxalate was dissolved in a slight excess of ammonia, and this solution, diluted to 100 cc., was electrolysed with a current of 0.25–1.5 amp. and 4–7 volts. The cathode with the deposited silver was dried cautiously over a low flame and thereafter ignited to incipient redness. The details of individual experiments are given in the table.

These results show plainly that the process of depositing silver from the ammoniacal solution of the oxalate, precipitated from the nitrate, is capable of yielding good

TABLE I.—The Electrolysis of Silver Nitrate Dissolved in Ammonium Oxalate and Ammonia.

	Ag in AgNO ₃ taken. Grm.	Ag found. Grm.	Error. Grm.	Current.			Time. Minutes.	Revolutions per minute.
				Ampères.	Approx. N.D.	Volt.		
A Crucible Used as Cathode.								
1.	0.2687	0.2685	−0.0002 (a)	1.5—1	5—3.3	6—7	25	500
2.	0.2687	0.2687	0.0000 (a)	1.5 1	5—3.3	6—7	30	500
3.	0.2687	0.2684	−0.0003 (a)	1—0.5	3.3—1.7	6—7	30	450
4.	0.2687	0.2685	−0.0002 (a)	1—0.5	3.3—1.7	4—6	30	450
5.	0.3183	0.3181	−0.0002 (a)	1.5—1	5—3.3	4—6	20	450
6.	0.3183	0.3178	−0.0005 (b)	1.5—1	5—3.3	4—6	10	450
Gauze Discs Used as Cathode.								
7.	0.3183	0.3179	−0.0004 (a)	1—0.5	0.5—0.25	4—6	20	400
8.	0.3183	0.3182	0.0001 (a)	1—0.25	0.5—0.10	6—8	25	400
9.	0.3183	0.3181	−0.0002 (a)	1—0.25	0.5—0.10	5—8	25	400
10.	0.3183	0.3180	−0.0003 (a)	0.75—0.25	0.4—0.10	5—7	40	450
11.	0.3183	0.3180	−0.0003 (a)	1—0.25	0.5—0.10	4—6	40	450
12.	0.3183	0.3176	−0.0007 (b)	0.75—0.25	0.4—0.10	6	20	450
Gauze Cone Used as Cathode.								
13.	0.2687	0.2686	−0.0001 (a)	1.5—1	3—2	4—6	25	500
14.	0.2687	0.2683	−0.0004 (a)	1—25	2—0.5	6—7	30	450
15.	0.2687	0.2684	−0.0003 (a)	1—5	2—1	4—6	25	450
16.	0.2687	0.2686	−0.0001 (a)	1—0.25	2—0.5	4—6	25	450
17.	0.5375	0.5373	−0.0002 (a)	1.5—1	3—2	6—7	25	450
18.	0.5375	0.5371	−0.0004 (a)	1.5—1	3—2	6—7	25	500

TABLE II.—The Electrolysis of Silver Chloride Dissolved in Ammonium Oxalate and Ammonia.

A Crucible Used as Cathode.								
1.	0.3191	0.3187	–0.0004	1.5–1	5–33	5–7	20	500
2.	0.3191	0.3189	–0.0002	1.5–1	5–33	4–6	30	500
Gauze Discs used as Cathode.								
3.	0.3191	0.3185	–0.0006 (c)	1.5–1	0.75–0.5	5–7	15	500
4.	0.3191	0.3189	–0.0002	1.5–1	0.75–0.5	5–7	25	500
5.	0.3191	0.3190	–0.0001	1.5–1	0.75–0.5	4–6	35	500

(a) Deposition complete, as shown by H₂S test.

(b) Deposition incomplete, as shown by H₂S test.

(c) Time of electrolysis short.

of a non-volatile nature can then be included in the deposit which after ignition consists of pure silver. The present paper describes the adaptation of this process to the quantitative estimation of silver.

The solutions of silver nitrate used in testing this process were carefully standardised by precipitating silver chloride from the hot solution by hydrochloric acid, cooling, digesting over night, and weighing the silver chloride upon asbestos after heating gently without melting. Depositions were made upon a rotating cathode of platinum—the ordinary crucible (Gooch and Medway, *American Journ.*

analytical results. Under the conditions of these experiments the electrolysis should be continued from twenty-five to thirty minutes in order to make sure that the deposition is complete. The deposit is naturally more adherent when the cathode surface is relatively large and the current density low. When the current density is high the deposit is apt to be voluminous, shrinking considerably upon drying, and this phenomenon was especially notable in the case of the deposits upon a comparatively small and smooth surface of the crucible. The best form of apparatus appears to be the gauze cone set point downward and so placed with relation to an annular platinum band used as the anode that the end of the axis where the centrifugal

* Contributions from the Kent Chemical Laboratory of Yale University (ccxvii.).

Effect of rotation is least shall not receive much of the deposit. Experiments made with stationary gauze electrodes were not successful, nor were those made with a dish cathode and stirring anode.

Other experiments in which the silver was first precipitated as silver chloride and then deposited from the solution in ammonia and ammonium oxalate are given in Table II. In these experiments, in which the solutions were more strongly ammoniacal than those of the experiments of the preceding series, the deposits were dark and spongy, but they became lighter in colour and more compact upon drying.

It appears, therefore, that silver may be deposited from an ammoniacal solution of the oxalate, in presence of ammonium nitrate or ammonium chloride, in pure condition and in form suitable for quantitative estimation.—*American Journal of Science*.

THE DETERMINATION OF MANGANESE BY THE SODIUM BISMUTHATE METHOD.*

By PAUL H. M.-P. BRINTON.

IN looking over the tables of analyses furnished by the Bureau of Standards at Washington with its analysed samples of steel, I noticed that the figures for manganese obtained by those chemists who used the sodium bismuthate method were in nearly all cases a little lower than the general averages obtained by all other methods. The differences were small, generally from 0.02 per cent to 0.03 per cent, but as I had noticed the same thing in using the bismuthate method myself, I had a curiosity to learn the cause of this tendency of the process. I have made a little series of analyses and experiments, the results of which may be of some interest, especially to those who have not yet adopted the method in regular work.

As is well known, the method depends upon the oxidation of manganese to permanganic acid by adding solid sodium bismuthate to the cold nitric acid solution of the sample. The excess of the bismuthate is filtered off on asbestos, a measured excess of ferrous ammonium sulphate solution added to the filtrate, and the latter then titrated back with potassium permanganate.

The method was originated by Schneider (*Dingl. Polytech.*, cclxix., 224), who used bismuth tetroxide, and subsequently developed by Reddrop and Ramage (*Journ. Chem. Soc.*, lxvii., 268; see also H. Ramage, *CHEMICAL NEWS*, lxxiv., 209), and by Brearley and Ibbotson (*CHEMICAL NEWS*, lxxxii., 269; lxxxiv., 247). Blair states that the sodium bismuthate method is not only remarkable in its simplicity and ease of manipulation (*Journ. Am. Chem. Soc.*, xxvi., 793; also "Chem. Anal. of Iron," 7th edit., 121 *et seq.*), but that for samples containing not over 2 per cent manganese it is the most accurate process known. The purpose of my work was to check up Blair's results (and those of the earlier workers also) and to confirm, if I could, his statement as to the accuracy of the method.

My analyses were made on various samples of the Bureau of Standards steels. I think we may take the averages given out by the Bureau, coming as they do from a variety of independent sources, as figures which represent the highest attainable accuracy in practical work. The methods and solutions were used, in the analyses of the steels, just as they are given by Blair. In the ferrous ammonium sulphate solution half the sulphuric acid was replaced by phosphoric acid, as suggested by Dr. C. B. Dudley. The end-point is rendered a little sharper by this modification as the colour due to the iron is less intense.

The solution of manganous sulphate for standardising the permanganate was carefully analysed, the manganese

being determined in weighed portions of the solution both as sulphate and as pyrophosphate. The results by these two methods were concordant.

The permanganate was standardised against the manganous sulphate solution, and also against pure Sørensen sodium oxalate, as well as against the "Sibley" standard iron ore issued by the Bureau of Standards. In standardising against the ore, the iron was reduced with amalgamated zinc in a Jones reductor. The titre obtained by the sodium oxalate was identical with that by the standard ore.

Five of the standard steels were analysed, the last one being a vanadium steel. Table I. shows a comparison between the results obtained by taking the strength of the permanganate as determined by the manganous sulphate method, and by taking it as determined by sodium oxalate or by the "Sibley" ore. In these determinations the theoretical conversion factors were used:— $\text{Na}_2\text{C}_2\text{O}_4$ to Mn 0.16024, and Fe to Mn 0.1967.

TABLE I.
Per cent manganese.

Bureau of Standards averages	0.412	0.916	0.760	0.568	0.669
Found with MnSO_4 as primary standard	0.410	0.922	0.757	0.557	0.663
Found with $\text{Na}_2\text{C}_2\text{O}_4$ or with iron ore as primary standard	0.411	0.920	0.758	0.562	0.665
	0.397	0.892	0.732	0.539	0.642
	0.398	0.890	0.733	0.544	0.644

From these figures it is seen that the results come somewhat low if the permanganate is standardised against sodium oxalate or against an iron compound, and the theoretical conversion factor used. It is interesting to note that the results in this table obtained by the latter method agree very closely with those obtained by the analysts who used the sodium bismuthate method in the analyses published by the Bureau of Standards with these samples. (The vanadium steel is an exception).

The results obtained by standardising the permanganate against the manganous sulphate solution are highly satisfactory, and a great many determinations which I have made in addition to those given in the table have convinced me that the degree of accuracy there shown can be regularly attained; and the process is so simple that no unusual manipulative dexterity is required to insure correct analyses. In fact it is hard to go wrong with the methods, after the correct titre for the permanganate is once obtained.

While standardising against a weighed quantity of manganous sulphate solution is the most accurate method known for the purpose here desired, it is also the most tedious. It requires a gravimetric determination of the manganese in the solution, and upon this result depends the accuracy of the whole process. A slight error made at this point introduces serious discrepancies in the final results.

The simplest method of standardising is against pure sodium oxalate; but since the figure obtained in this way brings the results too low we must use an empirical factor. The ratio $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ calls for the figure 0.16024, but to obtain correct results I find that the factor 0.1656 must be applied.

Since permanganic acid has a certain tendency to decompose in dilute nitric acid solution, particularly in the presence of much ferric nitrate, it was deemed advisable to investigate the rate of decomposition. Referring to the solution after the excess of bismuthate has been filtered off and when it is ready to receive the ferrous ammonium sulphate and be titrated back with permanganate, Blair says (*loc. cit.*):—"At a temperature of 5° C. the solution will remain unaltered for several hours, but at 40° C. fifteen minutes will show an appreciable change." The temperature of a laboratory is never so low as 5°, nor so high as 40°, so to see what danger from this decomposition would be if artificial cooling were not resorted to, I made the following series of determinations on the 0.760 per cent

* Read at the Minneapolis meeting of the American Chemical Society. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 4.

manganese steel from the Bureau of Standards. The temperature of room and solutions was 21° C.

TABLE II.

	Mn found (per cent).
1. Run strictly according to Blair. The filtration took about four minutes, and the ferrous ammonium sulphate was added and excess titrated immediately	0.760
2. Process same as before, except that after filtering an interval of twelve minutes was allowed before adding ferrous ammonium sulphate and titrating	0.758
3. Same, but an interval of twenty-five minutes was allowed	0.755
4. Same, but an interval of fifty-five minutes was allowed	0.750
5. Same, with an interval of ninety minutes	0.740

From these figures it appears that a delay of ten or fifteen minutes is practically without effect under ordinary conditions. Twenty-five minutes causes a slight lowering of the results, and a longer time than this has a decidedly unfavourable influence.

It may be mentioned in passing that a large excess of bismuthate is inadvisable, since it not only increases the cost of the process, but also tends to clog the filter rapidly, so that fewer filtrations can be made on the same asbestos felt. Just enough bismuthate should be used so that a slight excess is plainly visible in the bottom of the flask or beaker.

As regards the application of the method to iron ores low in manganese, I find the method advised by Blair, *i.e.*, treatment of the sample with 10 cc. water, 4 cc. H_2SO_4 , and 10–20 cc. HF in a platinum dish or crucible, somewhat tedious; and that it requires so large an amount of platinum if many samples are to be run is a further disadvantage. I prefer to dissolve the ore, about 1 gm., in 12 cc. of concentrated hydrochloric acid in a 4-oz. Erlenmeyer flask, evaporate almost to pastiness, and then add 4 cc. of concentrated sulphuric acid. By boiling down to heavy fumes over a free flame, manipulating the flask in a holder, the hydrochloric acid is so completely expelled that no test for chlorides can be obtained with silver nitrate. The residue is then taken up with 50 cc. of nitric acid, sp. gr. 1.135, and finished as usual. The process is quite rapid and the results very accurate. A few ores will not yield all their manganese to this treatment, so if the residue appears dark after taking up with nitric acid, it should be filtered off, fused with a very small amount of potassium bisulphate, and added to the main portion. It should be noted that this same treatment of the residue may be necessary with some ores even when using the hydrofluoric method of attack. The fact that the method as above given does not eliminate the silica is not really a drawback, since the silica is obtained in a form which does not seem to clog the filter much.

Attacking the ore by fusing with sodium peroxide was also tried, and it proved fairly successful. Were it possible to procure iron crucibles free from manganese this would be the ideal method. Since that seems to be impossible at present, I had to use nickel crucibles. It should be noted that some nickel contains traces of manganese, but not, I believe, as a rule. In using this method, 1 gm. of ore is fused with about 6 grms. of sodium peroxide at as low a heat as possible. A minute or two in liquid fusion is all that is necessary. The crucible and contents are treated with water in a covered beaker, and when the action is over the crucible is removed and one-third the volume of concentrated nitric acid added. The solution is boiled until all hydrogen peroxide is decomposed and everything dissolved but some manganese dioxide which has been precipitated. Ferrous sulphate is added until the manganese is reduced, the lower oxides of nitrogen are boiled off, and the analysis is finished as usual. The crucible is considerably attacked, but if the heat is kept low a dozen fusions may be made in a crucible before it is

unfitted for further use. The colour, due to the nickel, tends to obscure the end-point with permanganate somewhat, but after a little practice the point can be readily seen.

Summary.

1. Corroboration of Blair's statement that for small amounts of manganese the bismuthate is the most accurate method known.

2. When the potassium permanganate is standardised against sodium oxalate or iron, and the titre theoretically calculated, the results come out too low. A gravimetrically standardised manganous sulphate solution is the correct primary standard, but as this method is more inconvenient than the sodium oxalate method, it is suggested that pure Sørensen sodium oxalate be used, and that the empirical factor 0.1656, and not the theoretical factor 0.16024, be used in the conversion of the sodium oxalate figure to that for manganese.

3. The decomposition of ores by the hydrochloric and sulphuric acids method is suggested as being fully as accurate, more rapid, and perhaps more convenient than the hydrofluoric and sulphuric acids method. Fusing the ore with sodium peroxide is recommended as a method suitable for refractory ores.

NOTICES OF BOOKS.

Higher Mathematics for Chemical Students. By J. RIDDICK PARTINGTON, B.Sc. London: Methuen and Co., Ltd. 1911. (5s.).

THIS book contains a full course of mathematics for students of chemistry, including the elements of the calculus and differential equations. The book is illustrated entirely by examples drawn from chemistry, and many graphs and diagrams are provided. Examples are given for practice for the student, and others are worked out in the text. The treatment is as simple as possible, and the book should not be found unduly difficult for the use of the average student who has done only quite elementary work in geometry and algebra. In fact the author has, if anything, underestimated the amount of mathematical knowledge which his reader would in all probability possess; for instance, in an appendix the elementary theory of quadratic equations is discussed, and the principle of undetermined coefficients is explained. However, the chemical student who requires at a very moderate price a mathematical text-book which will help him to understand the application of mathematics to chemical problems, and to interpret correctly his experimental results, will probably be unable to do better than buy this book.

Lehrbuch der Mikrochemie. ("Text-book of Microchemistry"). By FRIEDRICH EMICH. Wiesbaden: J. F. Bergmann. 1911. (6.65 M.).

THIS book gives a *résumé* of the most important results which have been obtained in microchemistry, and will be specially acceptable as summarising for the first time all the quantitative data which have been collected. In order to keep within the very moderate limits of size which the author wished not to exceed, he has had to make a very careful selection of his material, and has wisely decided to include the most characteristic reactions of the common elements only. The book is intended for the use of specialists and not for beginners, and unnecessarily full detail has been avoided. In the first part the general methods of microchemistry are explained, and the apparatus employed is described and illustrated. The second part describes the reactions of the inorganic anions and cations, and also the most important results which have been obtained in the investigation of the derivatives of methane, benzene, and heterocyclic compounds. A tabular summary of microchemical reactions is provided, and copious references are given to the original literature of the subject.

CORRESPONDENCE.

CURIOUS THERMAL PHENOMENON.

To the Editor of the Chemical News.

SIR,—I noticed in a local paper the other day a report (source not given) that some French workmen had noticed that, when an iron bar is heated at one end and plunged into water nearly up to the other end that the latter, the previously cool part of the bar, becomes decidedly hotter. The paper said it was a well-known phenomenon to these iron workers; they had made up some sort of explanation about the cold water driving the heat along the bar. This might be a reasonable hypothesis on the corpuscular theory of heat, but hardly fits in with modern ideas.

My object in writing is to mention that I have myself noticed a very similar phenomenon, and, indeed, have tried to put the matter to the test with a thermometer long before I came across the above extract. Let anyone take an ordinary Berlin dish or metal basin, and heat it over a gas burner until the edges are so heated that it is just possible to hold the vessel with the fingers; now pour cold water into the centre of the dish till it is nearly full, and it will be found that a surprising increase of temperature occurs round the edge. Fancying that this apparent increase was more or less a nerve effect depending on the time the fingers had been in contact with the hot edges, I tried an iron bar with a hole drilled in it to receive a thermometer, the hole been filled with mercury. The end of the bar was bent at right angles and heated, the thermometer observed, and then the hot end of the iron cooled in a vessel of water; the result, however, was not in any way encouraging, perhaps because the conditions were not suitable.

I have succeeded, however, in showing that there is a *real increase* of temperature in another and very simple way. Cover a Berlin dish with a layer of melted paraffin-wax inside, and let it cool. Now heat it till the wax melts about three-quarters of the way up the sides; allow it to cool naturally, and observe that there is no appreciable fusion after the flame is removed. Repeat the experiment, but as soon as flame is removed half fill the dish with cold water, and it will be seen that there is a sudden extension of the melted zone towards the edges of the dish, proving undoubtedly that the temperature rises owing in some way to the cooling effect of the water on the central portion of the dish.

I have not seen this phenomenon mentioned in any work on heat, nor can I see any explanation of it. Perhaps some of your readers may have noticed this effect; perhaps also they may be able to give a satisfactory reason for it.—I am, &c.

E. G. BRYANT.

Grey Institute,
Port Elizabeth, S. Africa.

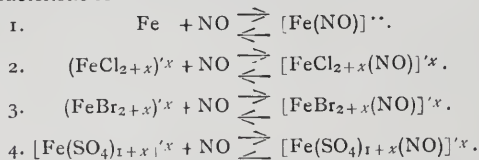
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 10, 1911.

Influence of the Medium and of Light upon the Decomposition of Quaternary Ammonium Salts.—E. Wedekind and F. Paschke.—The rate of spontaneous decomposition of quaternary aromatic ammonium halogen salts depends upon the nature of the solvent, some solvents, e.g., ethyl and methyl alcohol, retarding it, while others accelerate it. The influence of light is to be ascribed to thermic effects only. Free ammonium bases even in chloroform undergo no appreciable decomposition.

Metallic Nitroso-compounds.—V. Kohlschütter and P. Sazanoff.—The authors' experimental work on the metallic nitroso-compounds entirely confirms the results of Manchot. They find that all simple ferrous salts absorb NO, the amount absorbed being at the most one molecule of NO to one atom of iron. An intense brown colouration is produced by the absorption, and this absorption of light is characterised by a broad band in the yellow. The addition of a small amount of acid or salt to the solution of ferrous salt diminishes the absorption, probably owing to the normal effect on the ionisation. The following characteristic reversible reactions occur:—



And the stability of the nitroso-compounds of the complex anions is greater than that of the cation. The power of absorption of NO is increased by organic solvents. The copper nitroso-compounds resemble those of iron in all respects, but the power of absorption of the cupric cation for NO is smaller than that of iron.

Ferroso-ferric Oxide.—Siegfried Hilpert and Johannes Beyer.—When iron oxide is reduced by a mixture of hydrogen and water at 400° Fe₃O₄ is obtained. By raising the temperature and increasing the amount of water it is possible to obtain preparations which are richer in lower oxide. The processes occurring during reduction can be explained by assuming the formation of solid solutions.

MISCELLANEOUS.

Copper Water Pipes.—Mr. C. Ainsworth Mitchell in *Knowledge* for August comments on the request by the owners of a house in Paris for permission to instal copper instead of the usual leaden water-pipes for their water supply. It seems that the presence of sulphates in most drinking water renders the risk of poisoning insignificant, but if particularly soft water is supplied there may be trouble. The danger would be entirely obviated by the use of copper pipes, for although a dose of from fifty to one hundred milligrammes of copper sulphate is poisonous, the system can soon become acclimatised to a much greater quantity, while long before the poisonous dose has been reached, a liquid contaminated with copper acquires a harsh metallic taste which puts the consumer on his guard. With leaden pipes, however, a poisonous dose might be present in the water without its being detected by the taste, while it is well known that lead accumulates in the system.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Dicyanin—"Inquirer" would be obliged for any particulars or information as to where particulars may be obtained concerning the method of manufacture, chemical constitution and properties, and commercial uses of the dye known as dicyanin.

BOROUGH POLYTECHNIC INSTITUTE,
103, BOROUGH ROAD, LONDON, S.E.

CHEMISTRY DEPARTMENT.

The Governors invite applications for the Post of CHIEF ASSISTANT in the CHEMISTRY DEPARTMENT for Day and Evening Work. Commencing salary £150 to £170, according to qualifications and experience, rising to £250.

Conditions of Appointment may be obtained on application, marked "Chemistry," enclosing stamped addressed envelope, to

C. T. MILLIS, Principal.

THE CHEMICAL NEWS.

VOL. CIV., No. 2701.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

PORTSMOUTH, 1911.

INAUGURAL ADDRESS OF THE PRESIDENT,

Prof Sir WILLIAM RAMSAY, K.C.B., Ph.D., LL.D.,
D.Sc., M.D., F.R.S.

It is now eighty years since this Association first met at York, under the presidency of Earl Fitzwilliam. The object of the Association was then explicitly stated: "To give a stronger impulse and a more systematic direction to scientific inquiry, to promote the intercourse of those who cultivate science in different parts of the British Empire with one another and with foreign philosophers, to obtain a more general attention to the objects of science and a removal of any disadvantages of a public kind which impede its progress."

In 1831 the workers in the domain of science were relatively few. The Royal Society, which was founded by Dr. Willis, Dr. Wilkins, and others, under the name of the "Invisible, or Philosophical College," about the year 1645, and which was incorporated in December, 1660, with the approval of King Charles II., was almost the only meeting-place for those interested in the progress of science; and its *Philosophical Transactions*, begun in March, 1664-5, almost the only medium of publication. Its character was described in the following words of a contemporary poem:—

"This noble learned Corporation
Not for themselves are thus combined
To prove all things by demonstration
But for the public good of the nation,
And general benefit of mankind."

The first to have hived off from the Royal Society was the Linnean Society for the promotion of botanical studies, founded in 1788 by Sir James Edward Smith, Sir Joseph Banks, and other Fellows of the Royal Society; in 1807 it was followed by the Geological Society; at a later date the Society of Antiquaries, the Chemical, the Zoological, the Physical, the Mathematical, and many other Societies were founded. And it was felt by those capable of forming a judgment that, as well expressed by Lord Playfair at Aberdeen in 1885:—"Human progress is so identified with scientific thought, both in its conception and realisation, that it seems as if they were alternative terms in the history of civilisation." This is only an echo through the ages of an utterance of the great Englishman, Roger Bacon, who wrote in 1250 A.D.:—"Experimental science has three great prerogatives over all other sciences; it verifies conclusions by direct experiment; it discovers truths which they could never reach; and it investigates the secrets of Nature, and opens to us a knowledge of the past and of the future."

The world has greatly changed since 1831; the spread of railways and the equipment of numerous lines of steamships have contributed to the peopling of countries at that time practically uninhabited. Moreover, not merely has travelling been made almost infinitely easier, but communication by post has been enormously expedited and cheapened; and the telegraph, the telephone, and wireless telegraphy have simplified as well as complicated human existence. Furthermore, the art of engineering has made such strides that the question "Can it be done?" hardly arises, but rather "Will it pay to do it?" In a word, the human race has been familiarised with the applications of science; and men are ready to believe almost anything, if brought forward in its name.

Education, too, in the rudiments of science has been introduced into almost all schools; young children are taught the elements of physics and chemistry. The institution of a Section for education in our Association (L) has had for its object the organising of such instruction, and much useful advice has been proffered. The problem is, indeed, largely an educational one; it is being solved abroad in various ways—in Germany and in most European States by elaborate Governmental schemes dealing with elementary and advanced instruction, literary, scientific, and technical; and in the United States and in Canada by the far-sightedness of the people; both employers and employees recognise the value of training and of originality, and on both sides sacrifices are made to ensure efficiency.

In England we have made technical education a local, not an Imperial question; instead of half a dozen first-rate institutions of University rank, we have a hundred, in which the institutions are necessarily understaffed, in which the staffs are mostly overworked and underpaid; and the training given is that not for captains of industry, but for workmen and foremen. "Efficient captains cannot be replaced by a large number of fairly good corporals." Moreover, to induce scholars to enter these institutions, they are bribed by scholarships, a form of pauperisation practically unknown in every country but our own; and to crown the edifice, we test results by examinations of a kind not adapted to gauge originality and character (if, indeed, these can ever be tested by examination), instead of, as on the Continent and in America, trusting the teachers to form an honest estimate of the capacity and ability of each student, and awarding honours accordingly.

The remedy lies in our own hands. Let me suggest that we exact from all gainers of University scholarships an undertaking that, if and when circumstances permit, they will repay the sum which they have received as a scholarship, bursary, or fellowship. It would then be possible for an insurance company to advance a sum representing the capital value, viz., £7,464,931, of the scholarships, reserving, say, 20 per cent for non-payment, the result of mishap or death. In this way a sum of over six million pounds, of which the interest is now expended on scholarships, would be available for University purposes. This is about one-fourth of the sum of twenty-four millions stated by Sir Norman Lockyer at the Southport meeting as necessary to place our University education on a satisfactory basis. A large part of the income of this sum should be spent in increasing the emoluments of the Chairs; for, unless the income of a professor is made in some degree commensurate with the earnings of a professional man who has succeeded in his profession, it is idle to suppose that the best brains will be attracted to the teaching profession. And it follows that unless the teachers occupy the first rank, the pupils will not be stimulated as they ought to be.

Again, having made the profession of a teacher so lucrative as to tempt the best intellects in the country to enter it, it is clear that such men are alone capable of testing their pupils. The modern system of "external examinations," known only in this country, and answerable for much of its lethargy, would disappear; schools of thought would arise in all subjects, and the intellectual as well as the industrial prosperity of our nation would be assured. As things are, can we wonder that as a nation we are not scientific? Let me recommend those of my hearers who are interested in the matter to read a recent report on Technical Education by the Science Guild.

I venture to think that, in spite of the remarkable progress of science and of its applications, there never was a time when missionary effort was more needed. Although most people have some knowledge of the results of scientific inquiry, few, very few, have entered into its spirit. We all live in hope that the world will grow better as the years roll on. Are we taking steps to secure the improvement of the race? I plead for recognition of the fact that progress in science does not only consist in accumulating information which may be put to practical

use, but in developing a spirit of prevision, in taking thought for the morrow; in attempting to forecast the future, not by vague surmise, but by orderly marshalling of facts, and by deducing from them their logical outcome; and chiefly in endeavouring to control conditions which may be utilised for the lasting good of our people. We must cultivate a belief in the "application of trained intelligence to all forms of national activity."

The Council of the Association has had under consideration the formation of a Section of Agriculture. For some years this important branch of applied science, borrowing as it does from botany, from physics, from chemistry, and from economics, has in turn enjoyed the hospitality of each of these sections, itself having been made a sub-section of one of these more definite sciences. It is proposed this year to form an Agricultural Section. Here there is a need of missionary effort; for our visits to our colonies have convinced many of us that much more is being done for the farmer in the newer parts of the British Empire than at home. Agriculture is, indeed, applied botany, chemistry, entomology, and economics; and has as much right to independent treatment as has engineering, which may be strictly regarded as applied physics.

The question has often been debated whether the present method of conducting our proceedings is the one best adapted to gain our ends. We exist professedly "to give a stronger impulse and a more systematic direction to scientific inquiry." The Council has had under consideration various plans framed with the object of facilitating our work, and the result of its deliberations will be brought under your attention at a later date. To my mind, the greatest benefit bestowed on science by our meetings is the opportunity which they offer for friendly and unrestrained intercourse, not merely between those following different branches of science, but also with persons who, though not following science professionally, are interested in its problems. Our meetings also afford an opportunity for younger men to make the acquaintance of older men. I am afraid that we who are no longer in the spring of our lifetime, perhaps from modesty, perhaps through carelessness, often do not sufficiently realise how stimulating to a young worker a little sympathy can be; a few words of encouragement go a long way. I have in my mind words which encouraged me as a young man, words spoken by the leaders of Associations now long past—by Playfair, by Williamson, by Frankland, by Kelvin, by Stokes, by Francis Galton, by Fitzgerald, and many others. Let me suggest to my older scientific colleagues that they should not let such pleasant opportunities slip.

Since our last meeting the Association has to mourn the loss by death of many distinguished members. Among these are:—

Dr. John Beddoe, who served on the Council from 1870 to 1875, who recently died at a ripe old age, after having achieved a world-wide reputation by his magnificent work in the domain of anthropology.

Sir Rubert Boyce, called away at a comparatively early age in the middle of his work, was for long a colleague of mine at University College, and was one of the staff of the Royal Commission on Sewage Disposal. The service he rendered science in combating tropical diseases is well known.

Sir Francis Galton died at the beginning of the year, at the advanced age of 89. His influence on science has been characterised by Professor Karl Pearson in his having maintained the idea that exact quantitative methods could—nay, must—be applied to many branches of science which had been held to be beyond the field of either mathematical or physical treatment. Sir Francis was General Secretary of this Association from 1863 to 1868; he was President of Section E in 1862, and again in 1872; he was President of Section H in 1885; but, although often asked to accept the office of President of the Association, his consent could never be obtained. Galton's name will always be associated with that of his friend and relative, Charles Darwin, as one of the most eminent and influential of English men of science.

Professor Thomas Rupert Jones, also, like Galton a member of this Association since 1860, and in 1891 President of the Geological Section, died in April last at the advanced age of 91. Like Dr. Beddoe, he was a medical man with wide scientific interests. He became a distinguished geologist, and for many years edited the *Quarterly Journal of the Geological Society*.

Professor Story Maskelyne, at one time a diligent frequenter of our meetings, and a member of the Council from 1874 to 1880, was a celebrated mineralogist and crystallographer. He died at the age of 88. The work which he did in the University of Oxford and at the British Museum is well known. In his later life he entered Parliament.

Dr. Johnstone Stoney, President of Section A in 1897, died on July 1, in his 86th year. He was one of the originators of the modern view of the nature of electricity, having given the name "electron" to its unit as far back as 1874. His investigations dealt with spectroscopy and allied subjects, and his philosophic mind led him to publish a scheme of ontology which, I venture to think, must be acknowledged to be the most important work which has even been done on that difficult subject.

Among our corresponding members we have lost Professor Bohr, of Copenhagen; Professor Brühl, of Heidelberg; Hofrat Dr. Caro, of Berlin; Professor Fittig, of Strassburg; and Professor van't Hoff, of Berlin. I cannot omit to mention that veteran of science, Professor Cannizzaro, of Rome, whose work in the middle of last century placed chemical science on the firm basis which it now occupies.

I knew all these men, some of them intimately; and, if I have not ventured on remarks as to their personal qualities, it is because it may be said of all of them that they fought a good fight and maintained the faith that only by patient and unceasing scientific work is human progress to be hoped for.

It has been the usual custom of my predecessors in office either to give a summary of the progress of science within the past year, or to attempt to present in intelligible language, some aspect of the science in which they have themselves been engaged. I possess no qualifications for the former course, and I therefore ask you to bear with me while I devote some minutes to the consideration of ancient and modern views regarding the chemical elements. To many in my audience part of my story will prove an oft-told tale; but I must ask those to excuse me, in order that it may be in some wise complete.

In the days of the early Greeks the word "element" was applied rather to denote a property of matter than one of its constituents. Thus, when a substance was said to contain fire, air, water, and earth (of which terms a childish game doubtless once played by all of us is a relic), it probably meant that they partook of the nature of the so-called elements. Inflammability showed the presence of concealed fire; the escape of "airs" when some substances are heated or when vegetable or animal matter is distilled no doubt led to the idea that these airs were imprisoned in the matters from which they escaped; hardness and permanence were ascribed to the presence of earth, while liquidity and fusibility were properties conveyed by the presence of concealed water. At a later date the "Spagyrics" added three "hypostatical principles" to the quadrilateral; these were "salt," "sulphur," and "mercury." The first conveyed solubility and fixedness in fire; the second, inflammability; and the third, the power which some substances manifest of producing a liquid, generally termed "phlegm," on application of heat, or of themselves being converted into the liquid state by fusion.

It was Robert Boyle, in his "Skeptical Chymist," who first controverted these ancient and medieval notions, and who gave the word "element" the meaning that it now possesses—the constituent of a compound. But in the middle of the seventeenth century had not advanced far enough to make this definition useful; for he was unable

to suggest any particular substance as elementary. And, indeed, the main tenet of the doctrine of "phlogiston," promulgated by Stahl in the eighteenth century, and widely accepted, was that all bodies capable of burning or of being converted into a "calx," or earthly powder, did so in virtue of the escape of a subtle fluid from their pores; this fluid could be restored to the "calces" by heating them with other substances rich in phlogiston, such as charcoal, oil, flour, and the like. Stahl, however false his theory, had at least the merit of having constructed a reversible chemical equation:—Metal—phlogiston=Calx; Calx+phlogiston=Metal.

It is difficult to say when the first element was known to be an element. After Lavoisier's overthrow of the phlogistic hypothesis, the part played by oxygen, then recently discovered by Priestley and Scheele, came prominently forward. Loss of phlogiston was identified with oxidation; gain of phlogiston, with loss of oxygen. The scheme of nomenclature (*"Méthode de Nomenclature Chimique"*), published by Lavoisier in conjunction with Guyton de Morveau, Berthollet, and Fourcroy, created a system of chemistry out of a wilderness of isolated facts and descriptions. Shortly after, in 1789, Lavoisier published his *"Traité de Chimie,"* and in the preface the words occur:—"If we mean by 'elements' the simple and indivisible molecules of which bodies consist, it is probable that we do not know them; if, on the other hand, we mean the last term in analysis, then every substance which we have not been able to decompose is for us an element; not that we can be certain that bodies which we regard as simple are not themselves composed of two or even a larger number of elements, but because these elements can never be separated, or rather, because we have no means of separating them, they act, so far as we can judge, as elements; and we cannot call them 'simple' until experiment and observation shall have furnished a proof that they are so."

The close connection between "crocus of Mars" and metallic iron, the former named by Lavoisier "oxyde de fer," and similar relations between metals and their oxides, made it likely that bodies which reacted as oxides in dissolving in acids and forming salts must also possess a metallic sub-stratum. In October, 1807, Sir Humphry Davy proved the correctness of this view for soda and potash by his famous experiment of splitting these bodies by a powerful electric current into oxygen and hydrogen on the one hand, and the metals sodium and potassium on the other. Calcium, barium, strontium, and magnesium were added to the list as constituents of the oxides, lime, barytes, strontia, and magnesia. Some years later Scheele's "dephlogisticated marine acid," obtained by heating pyrolusite with "spirit of salt," was identified by Davy as in all likelihood elementary. His words are:—"All the conclusions which I have ventured to make respecting the undecomposed nature of oxymuriatic gas are, I conceive, entirely confirmed by these new facts." "It has been judged most proper to suggest a name founded upon one of its obvious and characteristic properties, its colour, and to call it chlorine." The subsequent discovery of iodine by Courtois in 1812, and of bromine by Balard in 1826, led to the inevitable conclusion that fluorine, if isolated, should resemble the other halogens in properties, and much later, in the able hands of Moissan, this was shown to be true.

The modern conception of the elements was much strengthened by Dalton's revival of the Greek hypothesis of the atomic constitution of matter and the assigning to each atom a definite weight. This momentous step for the progress of chemistry was taken in 1803; the first account of the theory was given to the public with Dalton's consent in the third edition of Thomas Thomson's "System of Chemistry" in 1807; it was subsequently elaborated in the first volume of Dalton's own "System of Chemical Philosophy," published in 1808. The notion that compounds consisted of aggregations of atoms of elements, united in definite or multiple proportions, familiarised the

world with the conception of elements as the bricks of which the Universe is built. Yet the more daring spirits of that day were not without hope that the elements themselves might prove decomposable. Davy, indeed, went so far as to write in 1811:—"It is the duty of the chemist to be bold in pursuit; he must recollect how contrary knowledge is to what appears to be experience. . . . To enquire whether the elements be capable of being composed and decomposed is a grand object of true philosophy." And Faraday, his great pupil and successor, at a later date, 1815, was not behind Davy in his aspirations, when he wrote:—"To decompose the metals, to re-form them, and to realise the once absurd notion of transformation—these are the problems now given to the chemist for solution."

Indeed, the ancient idea of the unitary nature of matter was in those days held to be highly probable. For attempts were soon made to demonstrate that the atomic weights were themselves multiples of that of one of the elements. At first the suggestion was that oxygen was the common basis; and later, when this supposition turned out to be untenable, the claims of hydrogen were brought forward by Prout. The hypothesis was revived in 1842 when Liebig and Redtenbacher, and subsequently Dumas, carried out a revision of the atomic weights of some of the commoner elements, and showed that Berzelius was in error in attributing to carbon the atomic weight 12.25, instead of 12.00. Of recent years a great advance in the accuracy of the determinations of atomic weights has been made, chiefly owing to the work of Richards and his pupils, of Gray, and of Guye and his collaborators, and every year an International Committee publishes a table in which the most probable numbers are given on the basis of the atomic weight of oxygen being taken as 16. In the table for 1911, of eighty-one elements no fewer than forty-three have recorded atomic weights within one-tenth of a unit above or below an integral number. My mathematical colleague, Karl Pearson, assures me that the probability against such a condition being fortuitous is 20,000 millions to one.

The relation between the elements has, however, been approached from another point of view. After preliminary suggestions by Döbereiner, Dumas, and others, John Newlands in 1862 and the following years arranged the elements in the numerical order of their atomic weights, and published in the *CHEMICAL NEWS* of 1863 what he termed his law of octaves—that every eighth element, like the octave of a musical note, is in some measure a repetition of its forerunner. Thus, just as C on the third space is the octave of C below the line, so potassium, in 1863 the eighth known element numerically above sodium, repeats the characters of sodium, not only in its physical properties—colour, softness, ductility, malleability, &c.—but also in the properties of its compounds, which, indeed, resemble each other very closely. The same fundamental notion was reproduced at a later date, and independently by Lothar Meyer and Dmitri Mendeleeff; and to accentuate the recurrence of such similar elements in *periods*, the expression "the periodic system of arranging the elements" was applied to Newlands' arrangement in octaves. As everyone knows, by help of this arrangement Mendeleeff predicted the existence of then unknown elements, under the names of eka-boron, eka-aluminium, and eka-silicon, since named *scandium*, *gallium*, and *germanium*, by their discoverers, Cleve, Lecoq de Boisbaudran, and Winckler.

It might have been supposed that our knowledge of the elements was practically complete; that perhaps a few more might be discovered to fill the outstanding gaps in the Periodic Table. True, a puzzle existed and still exists in the classification of the "rare earths," oxides of metals occurring in certain minerals; these metals have atomic weights between 139 and 180, and their properties preclude their arrangement in the columns of the Periodic Table. Besides these, the discovery of the inert gases of the atmosphere, of the existence of which Johnstone Stoney's spiral curve, published in 1888, pointed a forecast, joined the elements like sodium and potassium, strongly electro-

negative, to those like fluorine and chlorine, highly electro-positive, by a series of bodies electrically as well as chemically inert, and neon, argon, krypton, and xenon formed links between fluorine and sodium, chlorine and potassium, bromine and rubidium, and iodine and caesium.

Including the inactive gases, and adding the more recently discovered elements of the rare earths, and radium, of which I shall have more to say presently, there are eighty-four definite elements, all of which find places in the Periodic Table, if merely numerical values be considered. Between lanthanum, with atomic weight 139, and tantalum 181 there are in the Periodic Table seventeen spaces; and although it is impossible to admit, on account of their properties, that the elements of the rare earths can be distributed in successive columns (for they all resemble lanthanum in properties), yet there are now fourteen such elements; and it is not improbable that other three will be separated from the complex mixture of their oxides by further work. Assuming that the metals of the rare earths fill these seventeen spaces, how many still remain to be filled? We will take for granted that the atomic weight of uranium, 238.5, which is the highest known, forms an upper limit not likely to be surpassed. It is easy to count the gaps; there are eleven.

But we are confronted by an *embarras de richesse*. The discovery of radio-activity by Henri Becquerel, of radium by the Curies, and the theory of the disintegration of the radio-active elements, which we owe to Rutherford and Soddy, have indicated the existence of no fewer than twenty-six elements hitherto unknown. To what places in the Periodic Table can they be assigned?

But what proof have we that these substances are elementary? Let us take them in order.

Beginning with radium, its salts were first studied by Madame Curie; they closely resemble those of barium—sulphate, carbonate, and chromate insoluble; chloride and bromide similar in crystalline form to chloride and bromide of barium; metal, recently prepared by Madame Curie, white, attacked by water, and evidently of the type of barium. The atomic weight, too, falls into its place; as determined by Madame Curie, and by Thorpe, it is 89.5 units higher than that of barium; in short, there can be no doubt that radium fits the Periodic Table, with an atomic weight of about 226.5. It is an undoubted element.

But it is a very curious one. For it is *unstable*. Now, stability was believed to be the essential characteristic of an element. Radium, however, disintegrates—that is, changes into other bodies, and at a constant rate. If 1 grm. of radium is kept for 1760 years, only half a grm. will be left at the end of that time; half of it will have given other products. What are they? We can answer that question. Rutherford and Soddy found that it gives a condensable gas, which they named “radium-emanation”; and Soddy and I, in 1903, discovered that, in addition, it evolves helium, one of the inactive series of gases, like argon. Helium is an undoubted element, with a well-defined spectrum; it belongs to a well-defined series. And radium-emanation, which was shown by Rutherford and Soddy to be incapable of chemical union, has been liquefied and solidified in the laboratory of University College, London; its spectrum has been measured and its density determined. From the density the atomic weight can be calculated, and it corresponds with that of a congener of argon, the whole series being: helium, 4; neon, 20; argon, 40; krypton, 83; xenon, 130; unknown, about 178; and niton (the name proposed for the emanation to recall its connection with its congeners, and its phosphorescent properties), about 222.4. The formation of niton from radium would therefore be represented by the equation: radium (226.4) = helium (4) + niton (222.4).

Niton, in its turn, disintegrates, or decomposes, and at a rate much more rapid than the rate of radium; half of it has changed in about four days. Its investigation, therefore, had to be carried out very rapidly, in order that its decomposition might not be appreciable while its properties were being determined. Its product of change was named

by Rutherford “radium A,” and it is undoubtedly deposited from niton as a metal, with simultaneous evolution of helium: the equation would therefore be: niton (222.4) = helium (4) + radium A (218.4). But it is impossible to investigate radium A chemically, for in three minutes it has half changed into another solid substance, radium B, again giving off helium. This change would be represented by the equation: radium A (218.4) = helium (4) + radium B (214.4). Radium B, again, can hardly be examined chemically, for in twenty-seven minutes it has half changed into radium C¹. In this case, however, no helium is evolved; only atoms of negative electricity, to which the name “electrons” has been given by Dr. Stoney, and these have minute weight which, although approximately ascertainable, at present has defied direct measurement. Radium C¹ has a half-life of 19.5 minutes; too short, again, for chemical investigation; but it changes into radium C², and in doing so, each atom parts with a helium atom; hence the equation: radium C¹ (214.4) = helium (4) + radium C² (210.4). In 2.5 minutes, radium C² is half gone, parting with electrons, forming radium D. Radium D gives the chemist a chance, for its half-life is no less than sixteen and a-half years. Without parting with anything detectable, radium D passes into radium E, of which the half-life period is five days; and lastly, radium E changes spontaneously into radium F, the substance to which Madame Curie gave the name “polonium” in allusion to her native country, Poland. Polonium, in its turn, is half changed in 140 days with loss of an atom of helium into an unknown metal, supposed to be possibly lead. If that be the case, the equation would run: Polonium (210.4) = helium (4) + lead (206.4). But the atomic weight of lead is 207.1, and not 206.4; however, it is possible that the atomic weight of radium is 227.1, and not 226.4.

We have another method of approaching the same subject. It is practically certain that the progenitor of radium is uranium; and that the transformation of uranium into radium involves the loss of three alpha particles; that is, of three atoms of helium. The atomic weight of helium may be taken as one of the most certain; it is 3.994, as determined by Mr. Watson, in my laboratories. Three atoms would therefore weigh 11.98, practically 12. There is, however, still some uncertainty in the atomic weight of uranium; Richards and Merigold make it 239.4; but the general mean, calculated by Clarke, is 238.0. Subtracting 12 from these numbers, we have the values 227.0, and 227.4 for the atomic weight of radium. It is as yet impossible to draw any certain conclusion.

The importance of the work which will enable a definite and sure conclusion to be drawn is this:—For the first time we have accurate knowledge as to the descent of some of the elements. Supposing the atomic weight of uranium to be certainly 239, it may be taken as proved that in losing three atoms of helium radium is produced, and if the change consists solely in the loss of the three atoms of helium, the atomic weight of radium must necessarily be 227. But it is known that β -rays, or electrons, are also parted with during this change; and electrons have weight. How many electrons are lost is unknown; therefore, although the weight of an electron is approximately known, it is impossible to say how much to allow for in estimating the atomic weight of radium. But it is possible to solve this question indirectly by determining exactly the atomic weights of radium and of uranium; the difference between the atomic weight of radium *plus* 12, *i.e.*, plus the weight of three atoms of helium, and that of uranium, will give the weight of the number of electrons which escape. Taking the most probable numbers available, *viz.*, 239.4 for uranium, and 226.8 for radium, and adding 12 to the latter, the weight of the escaping electrons would be 0.6.

The correct solution of this problem would in great measure clear up the mystery of the irregularities in the Periodic Table, and would account for the deviations from Prout's Law, that the atomic weights are multiples of

some common factor or factors. I also venture to suggest that it would throw light on allotropy, which in some cases at least may very well be due to the loss or gain of electrons, accompanied by a positive or negative heat-change. Incidentally, this suggestion would afford places in the Periodic Table for the somewhat overwhelming number of pseudo-elements, the existence of which is made practically certain by the disintegration hypothesis. Of the twenty-six elements derived from uranium, thorium, and actinium, ten, which are formed by the emission of electrons alone, may be regarded as allotropes or pseudo-elements; this leaves sixteen, for which sixteen or seventeen gaps would appear to be available in the Periodic Table, provided the reasonable supposition be made that a second change in the length of the periods has taken place. It is above all things certain that it would be a fatal mistake to regard the existence of such elements as irreconcilable with the periodic arrangement, which has rendered to systematic chemistry such signal service in the past.

Attention has repeatedly been drawn to the enormous quantity of energy stored up in radium and its descendants. That in its emanation, niton, is such that if what it parts with as heat during its disintegration were available, it would be equal to three and a half million times the energy available by the explosion of an equal volume of detonating gas—a mixture of one volume of oxygen with two volumes of hydrogen. The major part of this energy comes, apparently, from the expulsion of particles (that is, of atoms of helium) with enormous velocity. It is easy to convey an idea of this magnitude in a form more realisable by giving it a somewhat mechanical turn. Suppose that the energy in a ton of radium could be utilised in thirty years, instead of being evolved at its invariable slow rate of 1760 years for half-disintegration, it would suffice to propel a ship of 15,000 tons, with engines of 15,000 horse-power at the rate of 15 knots an hour, for thirty years—practically the lifetime of the ship. To do this actually requires a million and a half tons of coal.

It is easily seen that the virtue of the energy of the radium consists in the small weight in which it is contained; in other words, the radium-energy is in an enormously concentrated form. I have attempted to apply the energy contained in niton to various purposes; it decomposes water, ammonia, hydrogen chloride, and carbon dioxide, each into its constituents; further experiments on its action on salts of copper appeared to show that the metal copper was converted partially into lithium, a metal of the sodium column; and similar experiments, of which there is not time to speak, indicate that thorium, zirconium, titanium, and silicon are degraded into carbon; for solutions of compounds of these, mixed with niton, invariably generated carbon dioxide; while cerium, silver, mercury, and some other metals gave none. One can imagine the very atoms themselves, exposed to bombardment by enormously quickly moving helium atoms failing to withstand the impacts. Indeed, the argument *a priori* is a strong one; if we know for certain that radium and its descendants decompose spontaneously, evolving energy, why should not other more stable elements decompose when subjected to enormous strains?

This leads to the speculation whether, if elements are capable of disintegration, the world may not have at its disposal a hitherto unsuspected source of energy. If radium were to evolve its stored-up energy at the same rate that gun-cotton does, we should have an undreamt-of explosive; could we control the rate we should have a useful and potent source of energy, provided always that a sufficient supply of radium were forthcoming. But the supply is certainly a very limited one; and it can be safely affirmed that the production will never surpass half-an-ounce a year. If, however, the elements which we have been used to consider as permanent are capable of changing with evolution of energy; if some form of catalyser could be discovered which would usefully increase their almost inconceivably slow rate of change, then it is not too much

to say that the whole future of our race would be altered.

The whole progress of the human race has indeed been due to individual members discovering means of concentrating energy, and of transforming one form into another. The carnivorous animals strike with their paws and crush with their teeth; the first man who aided his arm with a stick in striking a blow discovered how to concentrate his small supply of kinetic energy; the first man who used a spear found that its sharp point in motion represented a still more concentrated form; the arrow was a further advance, for the spear was then propelled by mechanical means; the bolt of the crossbow, the bullet shot forth by compressed hot gas, first derived from black powder, later from high explosives; all these represent progress. To take another sequence: the preparation of oxygen by Priestley applied energy to oxide of mercury in the form of heat; Davy improved on this when he concentrated electrical energy into the tip of a thin wire by aid of a powerful battery, and isolated potassium and sodium.

Great progress has been made during the past century in effecting the conversion of one form of energy into others, with as little useless expenditure as possible. Let me illustrate by examples: A good steam-engine converts about one-eighth of the potential energy of the fuel into useful work; seven-eighths are lost as unused heat, and useless friction. A good gas-engine utilises more than one-third of the total energy in the gaseous fuel; two-thirds are uneconomically expended. This is a universal proposition; in order to effect the conversion from one form of energy into another, some energy must be expended uneconomically. If A is the total energy which it is required to convert; if B is the energy into which it is desired to convert A; then a certain amount of energy, C, must be expended to effect the conversion. In short, $A = B + C$. It is eminently desirable to keep C, the useless expenditure, as small as possible; it can never equal zero, but it can be made small. The ratio of C to B (the economic coefficient) should therefore be as large as is attainable.

The middle of the nineteenth century will always be noted as the beginning of the golden age of science; the epoch when great generalisations were made, of the highest importance on all sides, philosophical, economic, and scientific. Carnot, Clausius, Helmholtz, Julius Robert Mayer abroad, and the Thomsons, Lord Kelvin and his brother James, Rankine, Tait, Joule, Clerk Maxwell, and many others at home, laid the foundations on which the splendid structure has been erected. That the latent energy of fuel can be converted into energy of motion by means of the steam-engine is what we owe to Newcomen and Watt; that the kinetic energy of the fly-wheel can be transformed into electrical energy was due to Faraday, and to him, too, we are indebted for the re-conversion of electrical energy into mechanical work; and it is this power of work which gives us leisure, and which enables a small country like ours to support the population which inhabits it.

I suppose that it will be generally granted that the Commonwealth of Athens attained a high-water mark in literature and thought, which has never yet been surpassed. The reason is not difficult to find; a large proportion of its people had ample leisure, due to ample means; they had time to think, and time to discuss what they thought. How was this achieved? The answer is simple: each Greek Freeman had on an average at least five helots who did his bidding, who worked his mines, looked after his farm, and, in short, saved him from manual labour. Now, we in Britain are much better off; the population of the British Isles is in round numbers 45 millions; there are consumed in our factories at least 50 million tons of coal annually, and "it is generally agreed that the consumption of coal per indicated horse-power per hour is on an average about 5 lbs." (Royal Commission on Coal Supplies, Part I.). This gives seven million horse-power per year. How many man-power are equal to a horse-

power? I have arrived at an estimate thus:—A Bhutanese can carry 230 lb. *plus* his own weight, in all 400 lb., up a hill 4000 feet high in eight hours; this is equivalent to about one-twenty-fifth of a horse-power; seven million horse-power are therefore about 175 million man-power. Taking a family as consisting on the average of five persons, our 45 millions would represent nine million families; and dividing the total man-power by the number of families, we must conclude that each British family has, on the average, nearly twenty "helots" doing his bidding, instead of the five of the Athenian family. We do not appear, however, to have gained more leisure thereby, but it is this that makes it possible for the British Isles to support the population which it does.

We have in this world of ours only a limited supply of stored-up energy; in the British Isles a very limited one—namely, our coalfields. The rate at which this supply is being exhausted has been increasing very steadily for the last forty years, as anyone can prove by mapping the data given on page 27, Table D, of the General Report of the Royal Commission on Coal Supplies (1906). In 1870 110 million tons were mined in Great Britain, and ever since the amount has increased by three and a-third million tons a year. The available quantity of coal in the proved coalfields is very nearly 100,000 million tons; it is easy to calculate that if the rate of working increases as it is doing our coal will be completely exhausted in 175 years. But, it will be replied, the rate of increase will slow down. Why? It has shown no sign whatever of slackening during the last forty years. Later, of course, it must slow down, when coal grows dearer owing to approaching exhaustion. It may also be said that 175 years is a long time; why, I myself have seen a man whose father fought in the '45 on the Pretender's side, nearly 170 years ago! In the life of a nation 175 years is a span.

This consumption is still proceeding at an accelerated rate. Between 1905 and 1907 the amount of coal raised in the United Kingdom increased from 236 to 268 million tons, equal to six tons per head of the population, against three and a-half tons in Belgium, two and a-half tons in Germany, and one ton in France. Our commercial supremacy and our power of competing with other European nations are obviously governed, so far as we can see, by the relative price of coal; and when our prices rise, owing to the approaching exhaustion of our supplies, we may look forward to the near approach of famine and misery.

Having been struck some years ago with the optimism of my non-scientific friends as regards our future, I suggested that a committee of the British Science Guild should be formed to investigate our available sources of energy. This Guild is an organisation, founded by Sir Norman Lockyer, after his tenure of the Presidency of this Association, for the purpose of endeavouring to impress on our people and their Government the necessity of viewing problems affecting the race and the State from the standpoint of science; and the definition of science in this, as in other connections, is simply the acquisition of knowledge, and orderly reasoning on experience already gained and on experiments capable of being carried out, so as to forecast and control the course of events; and, if possible, to apply this knowledge to the benefit of the human race.

The Science Guild has enlisted the services of a number of men, each eminent in his own department, and each has now reported on the particular source of energy of which he has special knowledge.

Besides considering the uses of coal and its products, and how they may be more economically employed, in which branches the Hon. Sir Charles Parsons, Mr. Dugald Clerk, Sir Boverton Redwood, Dr. Beilby, Dr. Hele-Shaw, Prof. Vivian Lewes, and others have furnished reports, the following sources of energy have been brought under review:—The possibility of utilising the tides; the internal heat of the earth; the winds; solar heat; water-power; the extension of forests, and the use of wood and peat as fuels; and lastly, the possibility of controlling the undoubted but almost infinitely slow disintegration of the

elements, with the view of utilising their stored-up energy.

However interesting a detailed discussion of these possible sources of energy might be, time prevents my dwelling on them. Suffice it to say that the Hon. R. J. Strutt has shown that in this country at least it would be impracticable to attempt to utilise terrestrial heat from boreholes; others have deduced that from the tides, the winds, and water-power small supplies of energy are no doubt obtainable, but that, in comparison with that derived from the combustion of coal, they are negligible; nothing is to be hoped for from the direct utilisation of solar heat in this temperate and uncertain climate; and it would be folly to consider seriously a possible supply of energy in a conceivable acceleration of the liberation of energy by atomic change. It looks utterly improbable, too, that we shall ever be able to utilise the energy due to the revolution of the earth on her axis, or to her proper motion round the sun.

Attention should undoubtedly be paid to forestry, and to the utilisation of our stores of peat. On the Continent the forests are largely the property of the State; it is unreasonable, especially in these latter days of uncertain tenure of property, to expect any private owner of land to invest money in schemes which would at best only benefit his descendants, but which, under our present trend of legislation, do not promise even that remote return. Our neighbours and rivals, Germany and France, spend annually £2,200,000 on the conservation and utilisation of their forests; the net return is £6,000,000. There is no doubt that we could imitate them with advantage. Moreover, an increase in our forests would bring with it an increase in our water-power; for without forest land rain rapidly reaches the sea, instead of distributing itself, so as to keep the supply of water regular, and so more easily utilised.

Various schemes have been proposed for utilising our deposits of peat: I believe that in Germany the peat industry is moderately profitable; but our humid climate does not lend itself to natural evaporation of most of the large amount of water contained in peat, without which processes of distillation prove barely remunerative.

We must therefore rely chiefly on our coal reserve for our supply of energy, and for the means of supporting our population; and it is to the more economical use of coal that we must look, in order that our life as a nation may be prolonged. We can economise in many ways: By the substitution of turbine-engines for reciprocating engines, thereby reducing the coal required per horse-power from 4 to 5 lb. to 1½ or 2 lb.; by the further replacement of turbines by gas-engines, raising the economy to 30 per cent of the total energy available in the coal, that is, lowering the coal consumption per horse-power to 1 or 1½ lb.; by creating the power at the pit-mouth, and distributing it electrically, as is already done in the Tyne district. Economy can also be effected in replacing "beehive" coke ovens by recovery ovens; this is rapidly being done; and Dr. Beilby calculates that in 1909 nearly six million tons of coal, out of a total of sixteen to eighteen millions, were coked in recovery ovens, thus effecting a saving of two to three million tons of fuel annually. Progress is also being made in substituting gas for coal or coke in metallurgical, chemical, and other works. But it must be remembered that for economic use, gaseous fuel must not be charged with the heavy costs of piping and distribution.

The domestic fire problem is also one which claims our instant attention. It is best grappled with from the point of view of smoke. Although the actual loss of thermal energy in the form of smoke is small—at most less than a half per cent of the fuel consumed—still the presence of smoke is a sign of waste of fuel and careless stoking. In works, mechanical stokers which ensure regularity of firing and complete combustion of fuel are more and more widely replacing hand-firing. But we are still utterly wasteful in our consumption of fuel in domestic fires. There is probably no single remedy applicable; but the introduction of

central heating, of gas fires, and of grates which permit of better utilisation of fuel will all play a part in economising our coal. It is open to argument whether it might not be wise to hasten the time when smoke is no more by imposing a sixpenny fine for each offence; an instantaneous photograph could easily prove the offence to have been committed; and the imposition of the fine might be delayed until three warnings had been given by the police.

Now I think that what I wish to convey will be best expressed by an allegory. A man of mature years who has surmounted the troubles of childhood and adolescence without much disturbance to his physical and mental state, gradually becomes aware that he is suffering from loss of blood; his system is being drained of this essential to life and strength. What does he do? If he is sensible, he calls in a doctor, or perhaps several, in consultation; they ascertain the seat of the disease, and diagnose the cause. They point out that while consumption of blood is necessary for healthy life, it will lead to a premature end if the constantly increasing drain is not stopped. They suggest certain precautionary measures; and if he adopts them, he has a good chance of living at least as long as his contemporaries; if he neglects them, his days are numbered.

That is our condition as a nation. We have had our consultation in 1903: the doctors were the members of the Coal Commission. They showed the gravity of our case, but we have turned a deaf ear.

It is true that the self-interest of coal consumers is slowly leading them to adopt more economical means of turning coal into energy. But I have noticed and frequently publicly announced a fact which cannot but strike even the most unobservant. It is this: When trade is good, as it appears to be at present, manufacturers are making money; they are overwhelmed with orders, and have no inclination to adopt economies which do not appear to them to be essential, and the introduction of which would take thought and time, and which would withdraw the attention of their employees from the chief object of the business—how to make the most of the present opportunities. Hence improvements are postponed. When bad times come, then there is no money to spend on improvements; they are again postponed until better times arrive.

What can be done?

I would answer: Do as other nations have done and are doing; take stock annually. The Americans have a permanent Commission initiated by Mr. Roosevelt, consisting of three representatives from each State, the sole object of which is to keep abreast with the diminution of the stores of natural energy, and to take steps to lessen its rate. This is a non-political undertaking, and one worthy of being initiated by the ruler of a great country. If the example is followed here the question will become a national one.

Two courses are open to us; first, the *laissez-faire* plan of leaving to self-interested competition the combating of waste; or second, initiating legislation which, in the interest of the whole nation, will endeavour to lessen the squandering of our national resources. This legislation may be of two kinds: penal, that is, imposing a penalty on wasteful expenditure of energy-supplies; and helpful, that is, imparting information as to what can be done, advancing loans at an easy rate of interest to enable reforms to be carried out, and insisting on the greater prosperity which would result from the use of more efficient appliances.

This is not the place, nor is there the time, to enter into detail; the subject is a complicated one, and it will demand the combined efforts of experts and legislators for a generation; but if it be not considered with the definite intention of immediate action, we shall be held up to the deserved execration of our not very remote descendants.

The two great principles which I have alluded to in an earlier part of this address must not, however, be lost sight of; they should guide all our efforts to use energy economically. Concentration of energy in the form of

electric current at high potential makes it possible to convey it for long distances through thin and therefore comparatively inexpensive wires; and the economic coefficient of the conversion of mechanical into electrical, and of electrical into mechanical energy is a high one; the useless expenditure does not much exceed one-twentieth part of the energy which can be utilised. These considerations would point to the conversion at the pit-mouth of the energy of the fuel into electrical energy, using as an intermediary, turbines, or preferably gas-engines; and distributing the electrical energy to where it is wanted. The use of gas-engines may, if desired, be accompanied by the production of half-distilled coal, a fuel which burns nearly without smoke, and one which is suitable for domestic fires, if it is found too difficult to displace them and to induce our population to adopt the more efficient economical systems of domestic heating which are used in America and on the Continent. The increasing use of gas for factory, metallurgical, and chemical purposes points to the gradual concentration of works near the coal mines, in order that the laying-down of expensive piping may be avoided.

An invention which would enable us to convert the energy of coal directly into electrical energy would revolutionise our ideas and methods, yet it is not unthinkable. The nearest practical approach to this is the Mond gas-battery, which, however, has not succeeded, owing to the imperfection of the machine.

In conclusion, I would put in a plea for the study of pure science, without regard to its applications. The discovery of radium and similar radio-active substances has widened the bounds of thought. While themselves, in all probability, incapable of industrial application, save in the domain of medicine, their study has shown us to what enormous advances in the concentration of energy it is permissible to look forward, with the hope of applying the knowledge thereby gained to the betterment of the whole human race. As charity begins at home, however, and as I am speaking to the British Association for the Advancement of Science, I would urge that our first duty is to strive for all which makes for the permanence of the British Commonwealth, and which will enable us to transmit to our posterity a heritage not unworthy to be added to that which we have received from those who have gone before.

Obituary.—We regret to announce that Mr. Albert Cooper, a Director of Messrs. Cooper, Son, and Co., Ltd., died on the 19th instant, in his 71st year.

Ternary System $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.—E. S. Shepherd and G. A. Rankin.—The authors have made a study of the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ in order to throw light upon the constitution of Portland cement. In the binary system $\text{CaO}-\text{SiO}_2$ the addition of a little alumina always gives rise to the formation of tricalcium silicate. It is unstable at its melting-point, and is therefore not formed from a melt of its constituents. A new and unstable form of the orthosilicate has been observed; possibly it plays some part in the formation of Portland cement. The limits of the different phases which appear in the complete diagram of the ternary system $\text{CaO}.\text{Al}_2\text{O}_3.\text{SiO}_2$ have been established, and it has been shown that Portland cement clinker can consist of the five following combinations of the constituents, if equilibrium has been reached:—

I.	II.	III.
CaO	$3\text{CaO}.\text{SiO}_2$	$2\text{CaO}.\text{SiO}_2$
$3\text{CaO}.\text{SiO}_2$	$2\text{CaO}.\text{SiO}_2$	$3\text{CaO}.\text{Al}_2\text{O}_3$
$3\text{CaO}.\text{Al}_2\text{O}_3$	$5\text{CaO}.\text{Al}_2\text{O}_3$	$5\text{CaO}.\text{Al}_2\text{O}_3$
IV.	V.	
$2\text{CaO}.\text{SiO}_2$	$2\text{CaO}.\text{SiO}_2$	
$5\text{CaO}.\text{Al}_2\text{O}_3$	$2\text{CaO}.\text{Al}_2\text{O}_3.\text{SiO}_2$	
$\text{CaO}.\text{Al}_2\text{O}_3$	$\text{CaO}.\text{Al}_2\text{O}_3$	

They are conditioned by relatively small changes in the amounts of lime present.—*Zeit. Anorg. Chem.*, lxxi, No. 1.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

PORTSMOUTH, 1911.

By Prof. J. WALKER, D.Sc., F.R.S.,
President of the Section.

THEORIES OF SOLUTIONS.

TWENTY-ONE years ago the Chemistry Section of the British Association at its meeting in Leeds was the scene of a great discussion on the nature of solutions. It was my first experience of a British Association meeting, and I well remember the stimulating effect of the lively discussion on all who took part in it. To-day, speaking from the honourable position of President of the Section, I conceive I can do no better than indicate the position of the question at the present time. And this appears to me the more appropriate as our science has had this year to mourn the departure of van 't Hoff, the founder of the modern theory of solution, whose name will remain one of the greatest in theoretical chemistry—in time to come, it will, I think, be considered almost the greatest. He had expressed the hope that he might attend this meeting as he did that twenty-one years ago. The hope is not fulfilled; his activity is merged in the final equilibrium of death. But his ideas are part and parcel of the chemical equipment of every one of us, and we know that whatever form the fundamental conceptions of chemistry may assume, the quantitative idea of osmotic pressure will be to the theory of solution what the quantitative idea of the atom is to chemical composition and properties. For I must emphasise the fact that chemistry is essentially a quantitative science, and no chemical theory, no partial chemical theory even, can be successful unless its character is quantitative. To quote the words of Lord Kelvin: "I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely in your thoughts advanced to the stage of science."

A general theory of solutions must be applicable to all solutions—to those in which solvent and solute exist in practically mere intermixture, as well to those in which solute and solvent are bound together in what we cannot sharply distinguish from ordinary chemical union. Between these extremes all grades of binding between solvent and solute exist, and it may be well to give a few examples illustrating the various types of solution.

Where no affinity exists between solvent and solute, the solution is practically of the same type as a mixture of two gases which are without chemical action on each other. The solute is merely diluted by the solvent and retains its properties unchanged. An example of this type of solution may be found in the solution of one saturated hydrocarbon in another, say of pentane in hexane. On mixing the two liquids there is no evidence of union between them, the volume of the mixture is practically the sum of the volume of the components, the heat of solution is practically *nil*, the vapour pressure of each constituent is reduced merely as if by dilution with the other constituent, and so on. That there is some action between the two components even in this extreme case must be admitted, but it may be referred entirely to action of a physical kind, such as one finds on mixing one gas with another at considerable pressures. Action of a chemical nature is absent. If it be said that even saturated hydrocarbons have some chemical affinity for each other, recourse may still be had for examples to mixtures of two inactive elements, say, liquid argon and liquid krypton, where chemical affinity is non-existent.

At the other extreme we have such solutions as those of

sulphuric acid and water. Here there is every physical evidence of chemical union. The volume of the mixture is by no means the sum of the volumes of the components, the amount of heat evolved on mixing is very great, the separate liquids, which are practically non-conductors, yield on mixing a solution which is a good conductor, and so on. There is obviously here a great influence of the solvent water on the solute sulphuric acid, and this influence we can only account for by assuming that it is essentially chemical in character.

As the influence in such a case is necessarily reciprocal, then if even one of the constituents of the solution is inactive chemically there can plainly be no action of a chemical nature on mixing. Thus, no matter what solvent we take, it can exercise no action other than that of a physical kind on argon, say, which has been dissolved in it; and, again, if liquid argon is chosen as solvent no substance dissolved in it can be affected by it chemically, and we thus obtain only the properties of a physical mixture. It is convenient therefore to classify liquid solvents according to their chemical activity. The saturated hydrocarbons, which are chemically very inert, and, as their name paraffin implies, little disposed to chemical action of any kind, may be taken as typically inactive solvents, analogous to liquid argon. Water, on the other hand, as its numerous compounds (hydrates) with all kinds of substances testify, may be taken as a typically active solvent. The ordinary organic solvents exhibit intermediate degrees of activity.

For the purpose of illustrating the effect of solvents on a dissolved substance one may conveniently take a coloured substance in a series of colourless solvents. If the substance is unaffected by the solvent, we might reasonably expect the colour of the solution to be the same as the colour of the vapour of the substance at equal concentration. Iodine, for instance, gives rise to the familiar violet vapour. Its solution in carbon disulphide has a colour practically similar, but its solution in alcohol or water is of a brown tint quite different from the other. In the indifferent hydrocarbons and in chloroform the colour is like that in carbon disulphide, in methyl or ethyl alcohol it is brown. We conclude therefore roughly that iodine dissolved in saturated hydrocarbons, in chloroform, carbon tetrachloride and carbon disulphide is little affected by the solvent, whereas in water and the alcohols it is greatly affected, probably by way of combination, since in all the solvents two atoms of iodine seem to be associated in the molecule. That combination between the iodine and the active solvents has really occurred receives confirmation from the behaviour of iodine in dilute solution in glacial acetic acid. If the colour of this solution is observed in the cold it is seen to be brown, resembling in colour the aqueous solution. If the solution be now heated to the boiling-point, the colour changes to pink, which may be taken to indicate that the compound of iodine and acetic acid which is stable at the ordinary temperature becomes to a large extent dissociated at 100°.

Now, as I have said, a general theory of solution must be applicable to all classes of solution, and herein lies the importance of van 't Hoff's osmotic pressure theory. It applies equally to mixtures of gases, to mixtures of inert liquids, and to mixtures such as those of sulphuric acid and water; and it has the further advantage that so long as the solutions considered are dilute there are simple relations connecting the osmotic pressure with other easily measurable properties of the solutions. It has been unfortunately the custom to oppose the osmotic pressure theory of solution to the hydrate, or more generally the solvate, theory, in which combination between solute and solvent is assumed. The solvate theory is, in the first place, not a general theory, and in the second place it is perfectly compatible with the osmotic pressure theory. It is in fact with regard to a general theory of solutions on the same plane as the electrolytic dissociation theory of Arrhenius. This theory of ionisation applies to a certain class of solutions, those, namely, which conduct electricity,

and is a welcome and necessary adjunct in accounting for the numerical values of the osmotic pressure found in such solutions. Similarly the hydrate, or more generally the solvate, theory is applicable only to those solutions in which combination between solvent and solute occurs, and will no doubt in time afford valuable information with regard to the osmotic pressure, especially of concentrated solutions in which the affinity between solvent and solute is most evident. It can tell us nothing about solutions in which one, or both, components is inactive, just as the electrolytic dissociation theory can tell us nothing about solutions which do not conduct electricity.

The great practical advantage bequeathed to chemists by the genius of van't Hoff is the assimilation of substances in dilute solution to substances in the gaseous state. Here all substances obey the same physical laws, and a secure basis is offered for calculation connecting measurable physical magnitudes, irrespective of the chemical nature of the substances and of the solvents in which they are dissolved, provided only that the solutions are non-electrolytes. If the solutions are electrolytes, the dissociation theory of Arrhenius, developed independently of the osmotic pressure theory of van't Hoff, gives the necessary complement, and for aqueous solutions offers a simple basis for calculation. Van't Hoff has given to science the numerically definable conception of osmotic pressure; Arrhenius has contributed the numerically definable conception of coefficient of activity of electrolytes in aqueous solution, or what is now called the degree of ionisation.

Of late there has been a tendency in some thermodynamical quarters to belittle the importance of the conception of osmotic pressure. It is quite true that from the mathematical thermodynamical point of view it may be relegated to a second place, and even dispensed with altogether, for it is thermodynamically related to other magnitudes which can be substituted for it. But it may be questioned if without the conception the cultivators of the thermodynamic method would ever have arrived at the results obtained by van't Hoff through osmotic pressure. Van't Hoff was only an amateur of thermodynamics, but the results achieved by him in that field are of lasting importance, and his work and the conception of osmotic pressure have given a great stimulus to the cultivation of thermodynamics to chemistry.

And here we trench on a question on which a certain confusion of thought often exists. To the investigator it is open to choose that one of several equivalent methods or conceptions which best suits his personal idiosyncrasy. To the teacher such a choice is not open. He must choose the method or conception which is most clearly intelligible to students, and is at the same time least likely to lead to misconception. Osmotic pressure is a conception which the chemical student of mediocre mathematical attainments can grasp, and it is not difficult to teach the general elementary theory of dilute solutions by means of it and of reversible cycles without liability to radical error or misconception. I should be sorry on the other hand to try to teach the theory of solutions to ordinary chemical students by means of any thermodynamic function. The two methods are thermodynamically equivalent, and the second is mathematically more elegant and in a way simpler, but it affords less opportunity than the first for the student to submit his methods to any practical check or test, and in nine cases out of ten would lead to error and confusion. The difficulty of the student is not the mathematical one; with the excellent teaching of mathematics now afforded to students of physics and chemistry the mathematical difficulty has practically disappeared—the difficulty lies in critically scrutinising the conditions under which each equation used is applicable.

Of the mechanism of osmotic pressure we still know nothing, but with the practical measurement of osmotic pressure great advances have been made in recent years. In particular the admirable work of Morse and Fraser is of the first importance in establishing for solutions up to normal concentration the relationship between osmotic

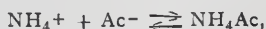
pressure and composition, and its variation with the temperature. Much may be anticipated from the continuation of these accurate and valuable researches, the experimental difficulties of which are enormous.

We are indebted to America not only for these researches, and for the voluminous material of H. C. Jones and his collaborators dealing with hydrates in solution, but also to A. A. Noyes and his school for accurate experimental work and for systematic treatment of solutions on the theoretical side. They, and also van Laar, have shown how solutions not coming within the ordinary range of dilute solutions to which van't Hoff's simple law is applicable, may in some cases at least be made amenable to mathematical treatment. Van't Hoff chose one simplification of the general theory by considering only very dilute solutions, for which very simple laws hold good, just as they do for dilute gases. Even a single gas in the concentrated or compressed form diverges widely from the simple gas laws; much more then may concentrated solutions diverge from the simple osmotic pressure law. The other simplification is to consider solutions of which the components are miscible in all proportions and are without action on each other; and this method has been developed with marked success from the point of view of osmotic pressure and other colligative properties.

The outstanding practical problem in the domain of electrolytic solutions is to show why the strong electrolytes are not subservient to the same laws as govern weak electrolytes. If we apply the general mass-action law of chemistry to the electrically active and inactive parts of a dissolved substance (the ions and un-ionised molecules) as deduced from the conductivities by the rule of Arrhenius, we find that for a binary substance a certain formula connecting concentration and ionisation should be followed, a formula which we know by the name of Ostwald's dilution law. This law seems to be strictly applicable to solutions of feeble electrolytes, but to solutions of strong electrolytes it is altogether without application. Wherein lies the fundamental difference between these two classes of solutions? Two kinds of explanation may be put forward. First, the ionised proportion may not be given accurately for strong electrolytes by the rule of Arrhenius; or second, the strong electrolytes do not obey the otherwise general law of active mass, which states that the activity of a substance is proportional to its concentration. The first mode of explanation has been practically abandoned, for other methods of determining ionisation give values for strong electrolytes in sufficient agreement with the values obtained by the method of Arrhenius. The other explanation is that for some reason the law of active mass is, apparently or in reality, not obeyed by some or all of the substances in a solution of a strong electrolyte. An apparent disobedience to the law of mass-action would, for example, be caused by the formation of complexes such as Na_2Cl_2 , or Na_2Cl^+ or NaCl_2^- in a solution of sodium chloride. Mere hydration, *e.g.* the formation of a complex $\text{NaCl}_2\cdot\text{H}_2\text{O}$, would not affect the mass-action law in dilute solution, and the electrolyte would obey the dilution law in solutions of the concentration usually considered. A somewhat similar explanation, which takes into account the properties of the solvent, is that the ionising power of the solvent water undergoes a noticeable change when the concentration of the ions in it increases beyond a certain limit.

I should wish now to draw attention to a point of view which has not, so far as I am aware, been fully considered. To begin with we may put to ourselves the question: Is it the ions in the solution which are abnormal or is it the non-ionised substance? A simple consideration would point at once to it being the non-ionised portion. We have, for example, in acetic acid a substance which behaves normally, so that the ions H^+ and Ac^- as well as the undissociated molecule HAc are normal. Similarly in ammonium hydroxide the ions NH_4^+ and OH^- as well as the non-ionised NH_3 and NH_4OH all behave normally. When we mix the two solutions there is produced a substance, ammonium acetate, which behaves abnormally.

Now, on the assumption that the equilibrium we are now dealing with is



which of these molecular species is abnormal in the relation between its concentration and its activity? Probably not the ions NH_4^+ and Ac^- , because these were found to act normally in the solutions of acetic acid and ammonia. The presumption is rather that the abnormal substance is the undissociated ammonium acetate, for this occurs only in the abnormal acetate solution, and not in the normal acetic acid and ammonia. This view, that it is the non-ionised portion of the electrolyte which exhibits abnormal behaviour, and not the ions, has been reached on other grounds by Noyes and others, and I hope in what follows to deduce reasons in its support.

One is apt, because the ions are in general the active constituents of an electrolyte, to lay too much stress on their behaviour in considering the equilibrium in an electrolytic solution. We are justified in attributing the fact that acetic acid is a weak acid, whilst trichloroacetic acid is a powerful one, rather to the properties of the un-ionised substances than to the properties of the ions. The divergence of trichloroacetic acid from the simple dilution law may similarly be due to an inherent property of the un-ionised acid, a single cause being not improbably at the bottom of both the great tendency to split into ions in water and also the abnormal behaviour towards dilution.

However that may be, I think the following reasoning goes far to show that the non-ionised portion of the electrolyte is that which is primarily abnormal in its behaviour, the ions acting in every way as normal. The dilution formulæ of Ostwald or of van't Hoff is essentially equilibrium formulæ. One side of the equilibrium represents the interaction of the ions to form the non-ionised substance, the other side represents the splitting up of the non-ionised substance into ions. In order to fix our ideas, we may consider a salt which obeys the empirical dilution-formula of van't Hoff. If c_u represents the molar concentration of the un-ionised portion, and c_i the molar concentration of each ion, then according to van't Hoff's empirical formula,—

$$\frac{c_i^2}{c_u} = \text{const.}$$

If the law of mass-action were obeyed we should have, on the other hand, Ostwald's dilution formula—

$$\frac{c_i^2}{c_u} = \text{const.}$$

According to this last formula, the activity of each substance concerned varies directly as its molar concentration, and a normal result is obtained on dilution. According to van't Hoff's formula as stated above, the activity of none of the substances concerned varies directly as its concentration; but since the constancy of the expression is the only test of its accuracy, there are obviously other methods of stating the relation which will throw the abnormal behaviour either on the ions or on the non-ionised substance. Thus, if we write the equivalent form—

$$\sqrt{\frac{c_i^2}{c_u}} = \text{const.}, \text{ or } \frac{c_i^{1.5}}{c_u} = \text{const.},$$

the un-ionised substance is here represented as behaving normally, and the ions abnormally; whilst if we write the formula in the form—

$$\frac{c_i^2}{c_u^{1.33}} = \text{const.},$$

the ions are represented as behaving normally, and the non-ionised substance abnormally. Now it is very important that a choice should be made amongst these three expressions, all equivalent amongst themselves so far as the mere constancy of the expression is concerned, as tested by measurements of electrolytic conductivity.

Looked at from the kinetic point of view we have in the first form,—

$$\frac{dx}{dt} = kc_i^2$$

$$- \frac{dx}{dt} = k'c_u$$

both direct and reverse actions abnormal. In the second form, we have—

$$\frac{dx}{dt} = kc_i^{1.5}$$

$$- \frac{dx}{dt} = k'c_u,$$

the ionisation being normal, the re-combination abnormal. And in the third form we have—

$$\frac{dx}{dt} = kc_i^2$$

$$- \frac{dx}{dt} = k'c_u^{1.33},$$

the ionisation being abnormal and the re-combination normal.

Now, if it were possible to measure directly the velocity of either ionisation or re-combination, we should at once be able to select the equilibrium formula which was really applicable. Unfortunately, such velocities are so high as to be beyond our powers of measurement. Yet it seems possible to seek and obtain an answer from reaction velocities which are measurable. One assumption must be made, but it seems to me so inherently probable that few will hesitate to make it. It is this, if a substance in a given solution has normal activity with respect to one reaction, it has normal activity with respect to all reactions in which it can take part in that given solution. Similarly, if a substance in a given solution exhibits abnormal activity with respect to one reaction, it will exhibit abnormal activity with respect to all.

Granting this assumption, we have then to find a reaction in which either the ionised or un-ionised portion of an abnormal electrolyte is converted into a third substance with measurable velocity. Such a reaction exists in the transformation of ammonium cyanate into urea in aqueous and aqueous-alcoholic solutions, which was investigated some years ago by myself and my collaborators, and found to proceed at rates which could easily be followed experimentally. First of all comes the question:—Is the urea formed directly from the ions or from the un-ionised cyanate? As Wegscheider pointed out, it is impossible from reaction-velocity alone to determine which portion passes directly into urea, if the velocities of ionisation and recombination are infinitely greater than that of the urea-formation, as is undoubtedly the case. Other circumstances make it highly probable that the ions are the active participants in the transformation, but we may leave the question open, and discuss the results on both assumptions.

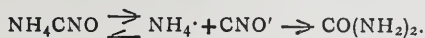
Suppose, first, that the un-ionised cyanate is transformed directly into urea. Then we have the successive reactions—



The slight reverse transformation of urea into cyanate may for the present purpose be neglected, as it in no way influences the reasoning to be employed.

If the un ionised substance behaves normally, then the conversion of the ammonium cyanate into urea, when referred to the un-ionised substance will appear unimolecular and obey the law of mass-action; when referred to the ionised substance it will not appear to be bimolecular, and will not obey the law of mass-action.

Suppose, now, that the direct formation of the urea is from the ions. Then we are dealing with the actions—



Again, let us assume the un-ionised substance to be normal. Once more, if the transformation is referred to the non-ionised substance it will appear as mono-molecular; when referred to the ionised substance it will not appear as bimolecular, as it should if the mass-action law were obeyed.

It is a matter of indifference, then, so far as the point with which we are dealing is concerned, whether the ionised or the non-ionised cyanate is transformed directly into urea. If the non-ionised cyanate behaves normally the action when referred to it will in either case appear to be strictly monomolecular.

If the ionised cyanate, on the other hand, behaves normally, the reaction when referred to it will be bimolecular and normal; when referred to the non-ionised cyanate will not be monomolecular, and therefore will be abnormal.

The actual experiments show that whether water or a mixture of water and alcohol be taken as solvent, the reaction when referred to the ions is strictly bimolecular; when referred to the non-ionised substance it is not monomolecular, *i.e.*, proportional to c_u , but rather proportional to a power of c_u other than the first, namely, $c_u^{-1.4}$.

This is, to my mind, a very strong piece of evidence that in the case of the abnormal electrolyte, ammonium cyanate, the abnormality of the ionisation equilibrium is to be attributed entirely to the non-ionised portion. But ammonium cyanate differs in no respect, with regard to its electrolytic conductivity from the hundreds of other abnormal binary electrolytes with univalent ions; and I am therefore disposed to conclude that it is to the non-ionised portion in general of these electrolytes that the abnormality is to be attributed.

As I have already indicated, this conclusion is not altogether novel, but in my opinion it has not been sufficiently emphasised. Even in discussions where it is formally admitted that the divergence from the dilution law may be due to the non-ionised portion, yet the argument is almost invariably conducted so as to throw the whole responsibility on the ions. The point which ought to be made clear is whether the constant k of the equation—

$$\frac{dx}{dt} = kc_i^2,$$

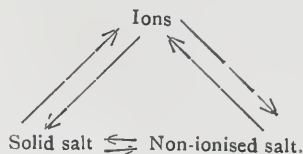
or the constant k' of the reverse equation—

$$-\frac{dx}{dt} = k'c_u,$$

is really constant. If the former, then the ions are truly normal, and primary explanations of the abnormality of the strong electrolytes can scarcely be sought in high total ionic concentrations and the like, though a connection between the two no doubt exists, both being determined by the same cause.

In my illustration I have assumed that there holds good a dilution law of the kind given by Storch, of which van't Hoff's dilution law is a particular case. Here the active mass is represented as a power of the concentration other than the first power. The argument I have used is altogether independent of this special assumption; the active mass of the abnormal substance may be any function of its concentration, and the same conclusion will be reached.

Nernst's principle of the constant ionic solubility product affords additional evidence that the ions act normally in solution. In deducing this principle it is generally assumed that it is the constant solubility of the non-ionised salt that determines the final equilibrium. This assumption, though convenient, is not necessary. The equilibrium is a closed one, thus:—



The solid is not only in equilibrium with the non-ionised salt but also with the ions. Now, in the deduction of the change of solubility caused by the addition of a substance having one ion in common with the original electrolyte the mass-action law for ionisation is assumed. This is of course justified when we deal with feeble electrolytes, but in the case of salts and strong acids which do not follow the mass-action law the experiments are found still to be in harmony with the theoretical deductions. This is not only so when the two substances in solution are both normal, but also when one is abnormal and the other normal, no matter which is used to produce the saturated solution. In fact, the principle of the constant ionic solubility product may be employed with equal success to calculate the effect on the solubility of one electrolyte of the addition of another electrolyte with a common ion, whether both electrolytes are normal, both abnormal, or whether one is normal and the other abnormal. At first sight, this apparent obedience of abnormal electrolytes to the mass-action law seems strange, but a little consideration shows that if it is only the non-ionised portion of a salt that is truly abnormal, the theoretical result is to be expected. Suppose that the ions do behave normally in the ionisation, then they must also act with normal active mass with reference to the solid, with which they may be regarded as in direct equilibrium according to the close scheme referred to above. A change, then, in the concentration of any one of the ions, brought about by the addition of a foreign salt with that ion, will necessarily bring about the change in solubility of the salt calculated from the mass-action law, so far at least as experiment can tell us, for any variation from theory is caused by the change in the nature of the solvent due to the addition of the foreign substance. We ought, then, on the assumption that the ions behave normally, to expect that the principle of the constant solubility product would yield results of the same degree of accuracy in dilute solutions whether the electrolytes considered were normal or abnormal. This, as I have said, is actually the case.

To put the whole matter briefly, in the equilibrium between electrolytes agreement will be obtained between theory and experiment whether we use the mass-action law, or an empirical law such as van't Hoff's dilution formula, provided only that we attribute the abnormality to the non-ionised portion of the electrolyte. Thus we can deduce the ordinary formulæ for hydrolysis or for isohydric solutions as readily for abnormal as for normal electrolytes, and find the most satisfactory agreement with experiment in both cases.

By this one simple assumption, then, for which I have offered some direct justification, it is possible to find a basis for calculation with abnormal electrolytes. The problem of *why* certain electrolytes should be normal and others abnormal is, of course, in no way touched by this assumption. That is a matter for further investigation and research.

Another great desideratum of the theory of solutions is to find a general basis for the calculation of hydrates. The present position of the theory of hydrates in solution may perhaps most aptly be compared to the theory of electrolytic dissociation for solvents other than water. That hydrates exist in some aqueous solutions is undoubted, but no general rule or method exists for determining what the hydrates are and in what proportions they exist. Similarly the theory of electrolytic dissociation applied to other than aqueous solutions affords no general means of determining what the ions are and how great is the degree of ionisation. It is only for aqueous solutions that Arrhenius

was able to give a practically realisable definition of degree of ionisation, and it is on this definition that the whole effective work on aqueous electrolytes is based; and until some general practically applicable principle of a similar character is attained for hydrates, the work done on that subject, however interesting and important it may be in itself, must necessarily be of an isolated character.

Arrhenius did not originate the doctrine of electrolytic dissociation or free ions: that was enunciated in 1857 by Clausius, and remained relatively barren. What he did was to introduce measurable quantities into the doctrine, and to show its simple quantitative applicability to aqueous solutions; immediately it became fertile. And as soon as a simple quantitative principle is developed for hydrates in solution, that doctrine will become fertile also.

It is surely now time that all the irrelevant and intemperate things that have been said and written by supporters of the osmotic pressure and electrolytic dissociation theories on the one hand, and by those of the hydrate theory on the other, should be forgotten. Far from being irreconcilable, the theories are complementary, and workers may, each according to his proclivity, pursue a useful course in following either. One type of mind finds satisfaction in using a handy tool to obtain practical results; another delights only in probing the ultimate nature of the material with which he works. For the progress of science both types are necessary—the man who determines exact atomic weights as well as the man who speculates upon the nature of the atoms. That the want of knowledge as to what the exact nature and mechanism of osmotic pressure is, should prevent accurate experimental work being done on it, or interfere with its use in theoretical reasoning, is equally ridiculous with the proposition that, because in the theory of osmotic pressure we have a good quantitative tool for the investigation of solutions, therefore we should abandon altogether the problem of its nature.

The fundamental ideas of a science are the gift to that science of the few great masters; the many journeymen investigators may be trusted to utilise them according to their abilities. Having once given his great principles to the world, van't Hoff remained practically a spectator of their development; but by his single act he provided generations of chemists with useful and profitable fields for their labour.

MISCELLANEOUS.

Action of Thionyl Chloride on Ethers of Acid Alcohols in Presence of a Tertiary Base.—G. Darzens.—When thionyl chloride acts on ethers of acid alcohols in presence of a tertiary base the hydrochloric ethers are obtained. Thus lactic ether is transformed into α -chloropropionic ether, and *l*-ethyl malate into *d*-ethyl monochlorosuccinate in presence of pyridine. This method of substituting chlorine for the alcoholic group OH is general, and is of great theoretical and practical importance.—*Comptes Rendus*, clii., No. 23.

NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 15th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Advertisement Manager as early as possible, but not later than the first post on TUESDAY, SEPTEMBER 12. Reserved spaces or special positions will be booked according to priority of application.

MACMILLAN'S NEW and RECENT BOOKS ON CHEMISTRY. CLASS BOOK OF CHEMISTRY.

By G. C. DONINGTON, M.A.

Part I., 1s. 6d. Parts II. and III., 2s. 6d.
Complete, 3s. 6d.

All the subjects included in the new syllabus in Chemistry for the Matriculation Examination of the University of London are dealt with in this book.

TECHNICAL JOURNAL.—"The book is one that can be strongly recommended for use as a class-book in schools."

THE TEACHER.—"The book has stood the best of all tests, viz., that of actual experience, and hence may be confidently recommended."

SCHOOL WORLD.—"The volume is most appropriate for classes in secondary schools and for junior classes in technical schools, and it possesses the advantage of meeting the requirements of both class-room and laboratory. The experiments are quite simple, and frequently exhibit novelty of method combined with improved efficiency. The illustrations are excellent."

THIRD EDITION.

NOW READY.

ESSAYS IN HISTORICAL CHEMISTRY

By Sir EDWARD THORPE,
C.B., LL.D., F.R.S., &c.

8vo. 12s. net.

Contains Lives of R. Boyle, J. Priestley, C. W. Scheele, H. Cavendish, J. Watt, A. L. Lavoisier, M. Faraday, T. Graham, F. Wöhler, J. B. A. Dumas, H. Kopp, V. Meyer, D. I. Mendeléeff, S. Cannizzaro, and J. Thomsen.

THIRD ENGLISH EDITION.

Theoretical Chemistry
from the Standpoint of Avogadro's Rule and Thermodynamics. By Professor WALTER NERNST, Ph.D. Revised in accordance with the Sixth German Edition by H. T. TIZARD. Third English Edition. 8vo. 15s. net.

Applied Electrochemistry.

By M. de KAY THOMPSON, Ph.D., Assistant Professor of Electrochemistry in the Massachusetts Institute of Technology. Illustrated. 8vo. 9s. net.

SECOND EDITION, completely Revised.

Inorganic Chemistry for Advanced Students. By the Rt. Hon. Sir HENRY ROSCOE, F.R.S., D.C.L., LL.D., and ARTHUR HARDEN, F.R.S., Ph.D. Second Edition, completely revised. With 53 Illustrations in Text. 4s. 6d.

SIXTH EDITION, thoroughly Revised.

Introduction to Physical Chemistry. By J. WALKER, LL.D., F.R.S. Sixth Edition. 8vo. 10s. net.

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. CIV., No. 2702.

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

A CHEMICAL analysis of over fifty wild plants can hardly be undertaken without learning something new concerning the numerous problems of vegetable physiology. A certain point of view is reached which enables one to survey the whole field comprehensively, and thereby not only to discover many facts never suspected before as well as numerous errors due to previous observers—errors based on an insufficiency of experiment and observation. The following are a few remarks suggested:—

Starch and Sugar of the Leaf.

The prevalent idea here seems to be that starch is the first product of assimilation; it is produced during the daytime and is converted by a ferment into sugar during the night. It is certain, however, that this view is open to serious doubt. In the first place, it is really difficult to detect the presence of starch at any time in the leaf. Who would formerly have believed the explicit statement lately made by M. D'Arbaumont (*Ann. Sci. Nat., Bot. ser.*, 1909), that from April till September the leaves of oak, beech, elder, birch, and of some forty-five other species of trees, shrubs, and herbs, contain no starch whatever? Moreover, numerous forms of chlorophyll flakes and granules of the leaf never apparently fabricate any starch, in certain species at all events. With regard to the conversion of starch into sugar by a ferment in the leaf, *i.e.*, into a reducing sugar more or less permanent, it is a remarkable fact that the quantity of glucose or maltose found in the vast majority of cases is extremely small. My own impression is, that the starch produced in the leaf is somehow or other thrown out of the protoplasm under the influence of light and warmth or other stimulant, and that it again, under adverse circumstances, is simply resorbed, unchanged or otherwise, into the protoplasm, and is not really a reserve-material liable to be drawn upon. True reserve starch does exist in roots, medullary rays, and in some leaves, but this is simply organic matter which the protoplasm in certain feeble conditions, or when it is artificially heated, fails to resorb. According to Brown and Morris (*Journ. Chem. Soc.*, 1898), "The first stages of the action on the starch-granules of a leaf are dependent upon the life of the protoplasm, but the hydrolysis of the starch-substance, when it has been brought down to the stage of soluble starch, is continued and finished by the enzyme." It would be very interesting to know what is meant here by "soluble starch," because repeated analysis clearly shows that in the leaf, living or dead, starch, as such, exists only in one and the same condition. No fresh leaf that I know of yields a solution of starch when merely boiled in water, and not very many when first dried and extracted successively by benzene, alcohol, water, and dilute soda, and it is only possible to explain this latter feat by the presence in such leaves (as, for instance, those of cleavers, pink campion, marsh-cinquefoil, willow herb, scabious, lesser celandine) of reserve starch strictly so-called, and as defined above. The inference drawn from repeated analyses is that sugar is a highly important product of assimilation, and that it is absolutely independent of starch, is not a respiratory material, and is not convertible into acids; there is evidence, moreover, that it migrates in the plant. Starch never does so.

Saponarin.

This constituent of certain plants has been variously pronounced to be a carbohydrate ("soluble starch"), an albuminoid, a tannin, and a tannoid. My attention was first called to it by an examination of the leaves of the garlic hedge-mustard (*Alliaria officinalis*) by the Sach's iodine method for starch. On placing the decolorised leaves in a solution of IKI, and washing with water, a peculiar purplish stain was observed on the sides of the basin which was obviously not due to starch. A fresh batch of leaves was dried and extracted with benzene, and then with alcohol. The latter extract in aqueous solution gave the following reactions, *viz.*, with iron salts a very dark brown colour; with chloride of tin and with acetate of lead, vivid yellow precipitates and colorations; with iodine, a deep violet flocculent precipitate, which on allowing to dry up turned red, but on adding a few drops of water a magnificent deep blue tint was immediately produced; on evaporating a solution of the extract and adding a few drops of glacial acetic acid and some HCl a splendid yellow colour was exhibited. Thus there remained no doubt that this mysterious substance was a tannoid or a glucoside of a flavone derivative, but distinguished from all others by the remarkable reaction with iodine, due apparently not to a pyrogallol nucleus, but to some form of oxybenzoic acid. It has no catechol or quinol nucleus, but probably a phloroglucol complex. I also obtained a large quantity of saponarin from the petals of foxglove, but there was none in the leaves of this plant, nor in those of shepherd's purse, bog asphodel, pink campion, timothy grass, tall fescue, bog bean, ragwort, &c. The fact of its occurrence in Cruciferae indicates a chemical relationship with the allied order Caryophyllaceae, in certain species of which it occurs in what may be called a typical quantity.

The Tannin of the Compositae.

This subject has been very little examined. M. Daniel has some notes upon it; and in 1882 Leppig stated that the tannin of tansy, $C_{23}H_{20}O_{31}$, is dark brown, faintly astringent, its aqueous solution yields with $FeCl_3$ a green precipitate, and boiled one hour with dilute HCl yields a catechin. My researches show that certain of the plants of this order contain a tannoid, while others contain a considerable quantity of coffee tannin. The tannoid is somewhat peculiar; it seems to contain a catechol and a quinol nucleus only, the former very pronounced but the latter doubtful. Its aqueous solution with a little ammonia added is coloured yellowish brown, and finally a very dark brown; it precipitates bromine water, but not IKI nor sulphate of quinine; its alcoholic solution acidified by HCl and pieces of metallic calcium thrown in apparently have no effect, but on adding excess of soda a deep green precipitate is thrown down, browning somewhat in air, and on now acidifying no red coloration (paracarthamine) is observed. It would seem, therefore, that metallic calcium does not react on these tannoids in the same way as sodium amalgam does under similar conditions. This tannoid is accompanied by, and is easily converted into a brownish catechin, soluble in alkalis to a brown red solution. The relation between these bodies and that very distinctive tannin named caffeetannin is not very clear. Nor does Corter's recent statement that caffeetannin is a mixture of two acids and other substances clear up the mystery. It does not appear, so far as I have observed, that the aforesaid tannoid and tannin ever coexist in the same species of Compositae; but apparently the sub-order Corymbiferae has most tannoid, the Cynarocephalae most tannin.

Nitrates and Chlorides.

Far too little attention has been paid to the highly suggestive remark of M. Pichard (*Comptes Rendus*, 1899, cxxviii., 615) to the effect that "the presence of chlorides in soil and their tendency to be absorbed by plants is antagonistic to the taking up of nitrates; and it is only owing to their predominance in the soil that nitrates can

be absorbed; their diminution in soil gives rise to increased absorption of chlorides." The following table, compiled from my own analyses, may be interesting in this connection. The mycorrhiza plants here mentioned contain no nitrates. The figures represent the percentage of chlorine in the crude ash minus charcoal:—

Mycorrhiza Plants.		Nitrate Plants.	
Wild hyacinth leaves	28	Nettle	2.9
Bog asphodel	17.5	Bogbean	1.2
Lesser celandine ..	12.8	Vetch	2.2
Daffodil	9.8	Reed	4
Primrose	17.2	Cow parsnip ..	2.5
Ramsons	21.5	Cleavers	3.9
Wood anemone ..	12	Willowherb ..	3.2
		Shepherd's purse ..	4.2

The above may be regarded as examples of extreme cases, and for the most part refer to the leaves of plants growing in meadows, open woodlands, or waste places. It does not, however, seem invariably to follow that a mycorrhiza plant should take up a large dose of chlorine, *e.g.*, valerian has mycorrhiza with 4.3 chlorine, gorse ditto with 2.7 chlorine, cuckoo-pint 1.6, &c. But, on the other hand, certain nitrate plants, although they never absorb an excessive dose thereof, manage occasionally to appropriate a pretty considerable amount; for example, foxglove 7.3 to 10.4, potato 6.5, bracken 10, burdock 5.8, polypody 7.6, goosefoot 7.2, &c. These plants, however, mostly inhabit dry or sandy places. According to Malaguti and Durocher (1858), ordinary plants growing on the edges of fields, hedges, and ditches have much chlorine, *i.e.*, in places where the soil nitrates are liable to be washed out. This explanation seems to account for the leaf ash of the common ragwort containing an unusual amount of chlorine, *viz.* 9.6 per cent, and that of the whole plant about the same; whereas groundsel contains less than 3 per cent. The latter is a strong nitrate plant.

Patterdale, Westmorland.

RADIO-ACTIVITY AS A KINETIC THEORY OF A FOURTH STATE OF MATTER.*

By Prof. WILLIAM H. BRAGG, M.A., F.R.S.

THERE are many points of resemblance between the movements of the molecules of a gas and the movements of those corpuscular radiations with which we have become acquainted in following up the discovery of radio-activity. In both cases we find that things of extremely minute dimensions are darting to and fro with great velocity; and in both cases the path of any one individual is made up of straight portions of various lengths, during which it is moving uniformly and free from external influence, and of encounters of short duration with other individuals, during which energy is exchanged and directions of motion are altered. There is even a resemblance in the universality of each movement. The motion of molecules is a fundamental fact throughout the whole of our atmosphere, and indeed in all material bodies; the motion of the radiant particles emitted by radio-active substances is also widely distributed, and of great importance. Taking Eve's estimate of the usual ionisation of the air we can calculate that in this room, in every second, some thousands of α - and β -particles enter into existence, complete their paths through all the atoms they meet, and sink into obscurity; some of them, *viz.*, the α -particles, as atoms of helium. Of these last some move through a range in air of just over 4 cm., an equal number have a range of just under 5 cm., and again an equal number move through 7 cm.; and the speed is so great that the life of each α -particle as such is completed in about a thousand-millionth of a

second. They leave their mark behind them in the ionisation of the air through which they have passed, and in the heat into which their energy has been commuted. The former effect is easily detected by the sensitive measuring instruments which we now possess; the latter is too small to measure, and must be greatly increased by the aid of radium itself before it can be investigated. But on a large scale which takes into account the distribution of radio-active material through the earth, the sea, and the air, the effects are of first rate importance to the physical conditions of our earth.

If we compare the movements a little more closely, we find differences as interesting as the resemblances. The motions which the kinetic theory of gases considers are those of the molecules of which gases consist: in the case of radio-activity, the things which move are quite different. They are sometimes electrons, which have come to be called β -rays when their speed is great, and cathode rays when it is somewhat less; or they are γ - or X-rays, which are new things to us; or if as α -particles they are helium atoms, such as we have known before, they move with excessive speeds which give them quite new properties. In general the radiant particles move hundreds of thousands of times as fast as the gas molecules do, and it is, no doubt, on account of this fact, as well as through their usually extreme minuteness, that their power of penetrating matter is so great. When two molecules of a gas collide, they approach within a fairly definite distance, which we call the sum of the radii of the molecules; and the approach is followed by a recession and new conditions of motion. Each molecule has, as it were, a domain into which no other molecule can penetrate. But the defences which guard the domain are of no account to the vigorous movements which we are considering now. The radiant particles pass freely through the atoms, and their encounters are rather with one or other of a number of circumscribed and powerful centres of force which exist within the atomic domain, and act with great power when and only when approached within distances which are small in comparison with the atomic radius. It is on this account that the new theory opens out to us such possibilities of discovering the arrangement of the interior of the atom. Never before have we been able to pass anything *through* an atom: our spies have always been turned back from the frontier. Now we can at pleasure cause to pass through any atom an α -particle, which is an atom of helium, or a β -particle, which is an electron, or a γ - or X-ray, and see what has happened to the particle when it emerges again: and from the treatment which it seems to have received we must try to find out what it met with inside.

The newer movement exists superimposed upon the other. Its velocities are so great that the gas (or liquid or solid) molecules are, in comparison, perfectly still. There is, as it were, a kinetic theory within a kinetic theory: there is a grosser movement of gas molecules which has long been studied, and in the same place and at the same time there is a far subtler and far more lively movement which is practically independent of the other. Your Vice-President, Sir William Crookes, was the first to find any trace of it. The behaviour of the cathode rays in the vacuum tubes which he had made showed him that he was dealing with things in no ordinary condition. Whatever was in motion was neither gas, nor solid, nor liquid, as ordinarily known, and he supposed it must be possible for matter to exist in a fourth state. We have gone far since Sir William's first experiments. The X-ray tube and radium have widely increased our knowledge of phenomena parallel to those of the Crookes tube. But I think we may still be glad to use Sir William's definition.

There is another very striking characteristic of the newer kinetic theory which differentiates it sharply from the older. The experiences of any one of the radiant particles in an atom which it crosses are quite unaffected by any chemical combination of that atom with others; that is to say, by any molecular associations it may have. Naturally,

* A Discourse delivered at the Royal Institution of Great Britain, January 27, 1911.

this simplifies investigation. We may no doubt ascribe this state of things to the fact that a radiant particle is concerned rather with the interior of the atom than with the exterior, and that it is the latter which is of importance in chemical action.

Let us take notice of one more important difference. The molecules of a gas move with velocities which vary at every collision, yet vary about a certain mean. But the peculiar motion of the radiant particle is only temporary. For only a very short time can any ray be described as matter in a fourth state; at the end of it the extraordinary condition has terminated, the particle has lost its tremendous speed or suffered some other change, and the ray ceases to exist. Speaking technically, we are dealing with initial not permanent conditions.

Let us now come back to resemblances between the two kinds of motion; for there is one point of similarity which is not quite so obvious as others I have mentioned, and is, I think, of the greatest importance; in fact, it is largely on account of this similarity that I have ventured to put the two theories together for comparison.

When the first experimenters in radio-activity allowed their streams of rays to fall upon materials of various kinds, they found that the irradiated surfaces were the sources of fresh streams of radiation. The secondary rays were sometimes of the same nature and quality as the primary, sometimes not. Further, they found that the secondaries, on striking material substances, could produce tertiaries, and so on. The examination of all the variations of this problem—the investigation of the consequences of changing the primary, of changing the substance, and last, but not least, of changing the form of the experimental arrangements—has been the cause of an enormous amount of work. There is a large literature dealing with secondary radiations of all kinds, which, I imagine, but few have read with any completeness, and the subject has become, on the surface at least, complicated and difficult. Now I believe that it is possible to clear away the greater portion of this complexity at a stroke, by the adoption of an idea which makes it possible to describe and discuss the whole of these phenomena in a very simple way. When an encounter takes place between two gas molecules, we suppose that the sum of the energies of the two is the same after the collision as before, and further, that there are just two things to consider—two molecules—after as well as before. I think that we may carry this idea over almost bodily to the newer theory. A radiant particle encounters an atom. The particle is a definite thing, it contains a definite amount of energy, and whether it is an α or β or γ or X-ray, its energy is to be found almost entirely inside a very minute volume. The encounter takes place. When it is over there are still two things, an atom and a radiant particle going away from it. The sum of the energies of the two is still the same, which means that we deny a possibility much considered at one time—viz., that in the encounter the atom could be made radio-active, and could unlock a store of energy usually unavailable. We suppose there is no energy to be considered except the original energy of the radiant particle, and we suppose that there are not now two or more radiant particles in place of the original one, which also is a limitation on previous ideas. It is a theory which ascribes a corpuscular form to all the radiations. Each particle, α , β , γ , or X, is to be followed from its origin to its disappearance, and we have nothing to think of but the one particle threading its way through the atoms. It loses energy as it goes, though little at any one collision, and it passes out of our reckoning when it has lost it all. There are no secondary radiations other than radiant particles moving in directions which are different from those in which they moved at first. Even when a cathode ray excites an X-ray in the ordinary Röntgen tube, or the X-ray excites a cathode ray in a manner almost as well known, it is hardly an exception to this rule. The cathode ray has an encounter with an atom and disappears; simultaneously the X-ray comes out of the atom, a circumscribed corpuscle carrying

on the energy of the cathode ray. There is a change, but it extends only to the external characteristics of the carrier of energy. The X-ray passes through the glass wall of the X-ray bulb, or at least it does so sometimes; it may pass through other matter as well, but sooner or later it has a fatal encounter with an atom, and the reverse change takes place. In all cases, in that of the undeviating α -ray, or the β -ray which suffers so many deflections, or the γ - or X-rays, it is a matter of tracing the movements of individual minute quantities of energy until they finally melt away.

Let us consider one or two simple experimental results from this point of view in order that we may illustrate this corpuscular theory, and at the same time may learn something of the properties of the corpuscles and of the arrangements of the atoms through which they pass.

We take first one of the simpler cases, the movement of an α -particle through a gas. The relatively large mass of the particle gives it an effectiveness which the other radiations do not possess. It moves straight through every atom it meets, and ionises most of them. Very rarely does it suffer any deflection from its course until its velocity is nearly run down. Then indeed it does appear to depart considerably from the straight path, and it may be that it is much knocked about by collisions before it finally comes to comparative rest. In this way we may explain the distribution of the ionisation along its path, which increases slowly at first and rapidly afterwards, until the α -particle has nearly finished its journey: it then falls off rapidly. Considering that the ionisation increases as the particle slows down and spends more time in each atom, and considering the more broken nature of the path near its end, the reason of these peculiarities is clear enough. Apart from its comparative simplicity, there are some other very interesting features of the particle's motion. It is found, for example, that the loss of energy which the particle incurs in crossing an atom is proportional to the square root of the atomic weight very nearly, and there is no certain explanation as yet of this curious law. And again, Geiger has examined the small scattering that does occur, and found that α -particles when moving quickly may be swung round completely even by the thinnest films of gold leaf, though the number is so small that the effect would have remained undetected had it not been for the scintillation method which he and Rutherford have perfected. He has found that about one particle in 8000 is returned in this way from a gold plate, which need consist only of a few thicknesses of gold leaf in order to give the maximum effect.

Now let us take an example from the behaviour of the β -rays. The β -particle is so light that it is easily deflected, even though it moves several times as fast as the heavier α -particle. Because it therefore possesses little energy its effects are much smaller, and no one has yet succeeded in handling a single β -particle in the same way as Rutherford and Geiger have handled the other. We are obliged to content ourselves with observations of the effects of a crowd of β -particles, since the combined action of many is necessary to give us an observable result. And at the same time that the β -particle gives much less effect than the α , it has a much more irregular course, so that the problem is doubly difficult. We are, in fact, only just beginning to understand it. There is a compensation in the fact that its very liability to deflection makes it all the more interesting an object. It is possible—and this is the particular β -ray problem I wish to consider now—to examine the deflection of a single β -particle by a single atom: the parallel result in the kinetic theory of gases has never, of course, been achieved.

Suppose that we project a stream of β -rays against a thin plate and measure the relative number sent back, which we do by measuring the ionisations caused by the incident and returned rays respectively. We do this for varying thicknesses of the plate, and plot the results, as, for example, Madsen has done. His plate was made of gold leaves, which could be had of extreme fineness,

From the relation thus obtained, it is possible to obtain with confidence the amount of β -radiation that would be returned by the thinnest plate that could be imagined, only one molecule thick. In such case the particles turned back could have had but one collision, and we have achieved our purpose. Madsen's figures show that a plate weighing 4 mmgrms. to the square centimetre turned back a tenth of the molecules that fell upon it, and as far as can be judged the ratio of the proportion turned back to the weight of the plate would be almost doubled for very thin plates. We might go more into detail, and find the distribution of those that are returned; we should then have data from which we might determine in some measure the distribution of the centres of force inside the atom. We cannot follow this up now, but I would like to draw your attention to a curious indication which we obtain when we compare the results for gold with those which Madsen found for aluminium. They show that the lighter metal turns back fewer β -particles, and that its power of absorbing a stream of rays is rather an absolute abstraction of energy. There is clearly an actual absorption effect, which is to be distinguished from the scattering effect. Indeed, the two effects are obviously of different importance in the two cases. When a β -ray strikes a gold atom it must be much more liable to deflection than when it strikes the lighter atom of aluminium. On the other hand, I think it can be shown clearly that in ploughing through aluminium atoms there is a relatively quicker absorption of energy. We may illustrate this by a rough model. Let us stand an electromagnet upright on the table, and let us suspend another magnet so that it can swing over the fixed one and just clear it. If we draw back the swinging magnet and let it go towards the fixed one, the currents running so that the two repel, then as the moving magnet tries to go by there will be a deflection depending on the relative speed, the closeness of approach, and the strength of the poles. This may represent the turning aside of an electron by a centre of force inside an atom. Now let the magnet at the table be supported by a spiral spring so as to be still upright, but have some freedom of motion; then, when the experiment is repeated, the swinging magnet pushes the other more or less to one side; it is less deflected, but it has to give up some of its energy. This is exactly what happens in the case of the β -particle. The centre of force in the gold atom behaves like the stiffer electromagnet on the table; it deflects the electron more, but robs it of less energy in doing so. It will not do to suppose the gold atom to differ from the aluminium atom simply in the number of centres of force, such as electrons, which it contains, if it is supposed that they all act independently. There is some other fundamental difference, equivalent to a difference in the stiffness with which the electrons are set in their places. There are two things to be expressed in the behaviour of the atom towards the β -particle, as has been pointed out several times. H. W. Schmidt has actually calculated them from experiments which gave them indirectly and somewhat approximately. The method I have just outlined gives one of them directly, viz., that which is called the scattering coefficient; and I think the other can also be found directly by a method which will serve as an illustration of the behaviour of γ -rays.

We must first, however, consider the part which γ - and X-rays play generally in this theory. Workers are by no means agreed as the proper way in which to regard them, but there is no need to enter at once on a discussion as to their nature. It is well known that they have the most extraordinary powers of penetration, and are unaffected by electric or magnetic fields. They have one property which alone, as I think, brings them within our experience; that is to say, the power of exciting β -rays from the atoms over which they pass. Were it not for this, they would still be unknown. When we examine this production of β -rays, we find that in the first place their speed depends on the quality of the γ -rays which cause them, and not on the nature of the atoms in which they arise; in the second,

that the β -rays to a large degree continue the line of motion of the γ -rays as if the latter pushed them out of the atoms; and, lastly, that the number of the β -rays depends on the intensity of the γ -rays. It is these facts which suggest the simple theory I have already described. The γ -ray is some minute thing which moves along in a straight line without change of form or nature, which penetrates atoms with far greater ease than the α or β -particle, which is not electrified, and which sooner or later disappears inside an atom, handing on a large share of its energy to a β -particle which takes its place. The absorption of γ -rays is simply the measure of their disappearance in giving rise to β -rays, one γ -ray producing one β -ray, and no more.

We find the same sort of scattering in the case of γ -rays as in that of β -rays. Of a stream of rays directed against a plate which it can penetrate easily, we find that a few are turned completely back, a very much larger number are only slightly turned out of their path, and the rest go on. The scattered rays are very similar to the original rays; there is no need to suppose that the original ray disappears to be replaced by a secondary, any more than there is to suppose that α - and β -rays disappear, and are replaced by others in similar cases. When therefore a γ -ray enters an atom three possibilities await it. The first is a negative one, it may go through the atom untouched, and this must happen in the majority of cases; the second chance is that of deflection, and the third that of conversion into a β -ray, using the word conversion in a general sense without going into details as to the nature of the process.

Now we may consider our γ -ray problem. Suppose a stream of these rays passing over a block of any substance such as aluminium, or zinc, or lead. When they are really penetrating rays they are equally absorbed by equal weights of these materials, which means that in equal weights equal numbers of β -rays springs into existence. If these β -rays were able to move through equal weights of the metals, we should find in each metal the same "density" of β -rays; and the important point is that this is independent of whether the rays are straight or crooked in their paths. If ten lines of given length were begun in every square centimetre of a sheet of paper, the ink used in drawing them would be independent of the straightness of the lines but proportional to their length. Now, if we make a cavity in each metal the β -rays will cross it in their movements to and fro; and if a little air is introduced into the cavity the ionisation produced in it will be a measure of the density of the β -rays, and therefore the average distance each moves in the metal. Experiment shows that we get twice as much ionisation in a cavity in the lead as in a similar cavity in the aluminium, and we conclude that the β -particle really has a longer track in the heavier metal. This experiment gives us the second constant of β -ray absorption; that is to say, the rate at which its energy is taken away from it; the other experiment gave the chance of deflection only. We see that the path of a β -ray in aluminium is more direct, but of less length than in lead; in the latter metal it has really a longer path, but it does not get so far away from its starting point because it suffers so many more deflections.

Finally, let us take a problem from the X-rays. Let us see how we may test the idea that X- and γ -rays do not ionise themselves, but leave all the work to be done by the β -rays which they produce. Suppose a pencil of X-rays to pass across a vessel and to produce ionisation therein. It is convenient to use, not the original X-rays, which are heterogeneous, but the rays which are scattered by a tin-plate on which the primary rays fall. Such "tin-rays," as we often call them briefly, are fairly homogeneous, and give cathode-rays of convenient penetration. In some experiments of mine the rays crossed a layer of oxygen 3.45 cm. wide, having a density 0.00137, and the ionisation produced was 227 on an arbitrary scale. The result may be put in the following way:—Suppose, provisionally, that all this ionisation is done indirectly; the oxygen

has converted so much X-ray energy into cathode-ray energy, and these cathode-rays penetrating their one or two millimetres of oxygen, which is all they can do, have ionised the gas. Then we may say that in crossing a layer of oxygen weighing 3.45×0.00137 , or 0.00473 grm. per sq. cm., enough cathode-rays have been produced to cause an ionisation of 227 units; and therefore that a layer weighing 1 mgrm. per sq. cm. would produce 48 units in the same way. We now proceed to compare this production in oxygen with the similar effect in a metal such as silver. Stretching a silver foil across the chamber in the path of the rays we find that under the same intensity of rays the ionisation is largely increased, and the change is due to cathode-rays which the X-rays have generated in the silver. Not all these rays get out of the silver, but we can overcome this difficulty by taking silver foils of different thickness, drawing a curve connecting the effect of the foils with their thicknesses, taking the curve back to the origin, and so finding what would be the effect of a foil so thin that all the cathode-rays did get out. In my case I found that a mgrm. of silver produced enough cathode-rays to give an ionisation 1580. This is thirty-three times as much as the oxygen could do. Now, according to our theory this should be because silver absorbs tin-rays thirty-three times more than oxygen does; and experiment showed this to be very nearly the case. In finding the absorbing power of oxygen I measured, first, those of carbon and oxalic acid, and then proceeded by calculation; for the absorption in a gas is difficult to determine.

Two interesting points appeared in this experiment. In the first place, the ratio between the two quantities of cathode-rays, which appear on the two sides of a silver leaf through which the "tin-rays" pass, is nearly constant for different thicknesses of leaf, and with the thinnest leaf obtainable each quantity was about half its full value. It would have been desirable to have had still thinner leaves; but it is fairly clear that the ratio would be nearly the same for extreme thinness. The cathode radiation, which appears on the side of the leaf whence the X-rays emerge, is 1.30 times that which appears on the other, and we may take it that this would be the case even if the leaf were but one atom thick. Thus, when an X-ray plunges into an atom in which its energy is converted into that of a cathode-ray, the cathode-ray may emerge at any point but there is a 30 per cent greater chance that it will more or less continue the line of motion of the X-ray than that it will not. In previous work on the conversion of γ -ray into β -ray energy, I have found that the β -ray may practically be supposed to continue the line of motion of the γ -ray, so that there is a great difference in behaviour of the two classes of ray in this respect. It is remarkable that the scattering of the γ -rays shows also a much greater dissymmetry than is found in the case of the X-rays. It looks as if the β -rays that appear when γ - or X-rays impinge on atoms are related rather to the scattered than to the unscattered primary rays. Putting it somewhat crudely, no doubt, it might be said that when a γ - or X-ray is deflected in passing through an atom, it runs a risk of being converted into a β -ray in the process, so that β -rays are found distributed about the atom in rough proportions to the secondary γ - or X-rays. In the case of γ -rays this practically amounts to their all going straight on at first; in the case of X-rays the distribution is more uniform.

Another interesting point arises in this way. When the X-rays from tin are allowed to pass into the ionisation chamber through increasing thicknesses of silver foil, the cathode rays grow at a rate which is not represented by the exponential curve usually assumed. The amount is for some time more nearly proportional to the thickness of the foil. A second foil adds its own effect without destroying much of the one on which it is laid. This may easily be ascribed to the relation of the ionisation due to the β -particle to the energy it has to spend. The ionisation is nearly all at the end of the path, and the second layer does not absorb the rays made in the first because they are still at the beginning of their career.

These few experiments which I have described may serve to illustrate both the justice and the convenience of placing all these rays, α , β , γ , and X, in one class. We are tempted to consider them all as corpuscular radiations of some sort, and we then look upon our researches into their behaviour as attempts to understand the collisions of the various new corpuscles with the constituent centres of force in the atoms. But if we ascribe corpuscular properties to the γ - and X-rays, we are led far away from the original speculations as to their nature. Stokes supposed them to be spreading ether pulses, but in his theory the energy of the pulse spreads on everwidening surfaces as the time passes, and is utterly insufficient to provide the energy of the β -rays which the γ - or X-rays excite. Some sort of mechanism has to be devised by which the energy of the γ -ray moves on without spreading, so that at the fateful moment it may be all handed over to the β -ray, which carries it on. I had the hardihood myself to propose a theory of this kind. My idea was that the γ - or X-ray might be considered as an electron which had assumed a cloak of darkness in the form of sufficient positive electricity to neutralise its charge. Nor do I see any reason for abandoning this idea, for it is at least a good working hypothesis. It means, of course, that not only does the energy of the β -ray come from the γ -ray, but the β -ray itself.

Many insist that my neutral corpuscle is too material, and that something more ethereal is wanted. For it appears that ultra-violet light possesses many of the properties of X- and γ -rays. It can excite electrons to motion, and sometimes the speed of the electron depends on the quality of the light and not on the nature of the material from which it springs. They propose, therefore, a quasi-corpuscular theory of light, γ - and X-rays being included. The immediate objection to this proposal is that it seems to throw away at once all the marvellous explanations of interference and diffraction which Young and Fresnel founded on a theory of spreading waves; and I do not think anyone has yet made good this defect. The light corpuscle which is proposed is a perfectly new postulate. It is to move with the velocity of light, keeping a circumscribed and invariable form, to have energy and momentum, and to be capable of replacing and being replaced by an electron which possesses the same energy but moves at a slower rate; and, of course, it has to do all that the old light-waves did. The whole situation is most remarkable and puzzling. We are working and waiting for some solution which, perhaps, will come in a moment unexpectedly. Meanwhile, we must just try to verify and extend our facts, and be content to fix together parts of the puzzle, since we cannot, as yet, manage the whole. My object to-night has been to show you how we may conveniently bind together a large number of the phenomena of radio-activity into an easily-grasped bundle, using a kinetic theory which has many points of resemblance to the older kinetic theory of gases.

A REVISION OF THE ATOMIC WEIGHT OF IRON.

FOURTH PAPER.—THE ATOMIC WEIGHT OF METEORIC IRON.

By GREGORY PAUL BAXTER,
and
THORBERGUR THORVALDSON.

So far as we know atomic weight investigations have always in the past been carried out with material of terrestrial origin. While there is no reason to believe that an extra-terrestrial element differs from the corresponding terrestrial element in any way, a comparison is at any rate worth while. (Such a comparison was suggested to one of us ten years ago by Prof. T. W. Richards, and independently through him more recently by Sir Henry Roscoe). As sensitive a means as any other for detecting

ATOMIC WEIGHT OF IRON.

Ag = 107.880.

Br = 79.916.

Series I.—FeBr₂ : 2Ag.

No. of analysis.	Weight of FeBr ₂ in vacuum. Grms.	Weight of Ag in vacuum. Grms.	Weight of Ag added or subtracted. Grm.	Corrected weight of Ag in vacuum. Grms.	Ratio, FeBr ₂ : 2Ag.	Atomic weight of iron.
1.	3.95460	3.95621	0.00010	3.95631	0.990568	55.835
2.	4.66954	4.67147	0.00030	4.67177	0.999523	55.825
3.	4.75335	4.75530	0.00020	4.75550	0.999548	55.831
4.	6.95582	6.95894	-0.00040	6.95854	0.999609	55.844
5.	3.20762	3.20864	0.00040	3.20904	0.999557	55.833
Average					0.999561	55.834
Average, rejecting Nos. 2 and 3					0.999578	55.837

Series II.—FeBr₂ : 2AgBr.

No. of analysis.	Weight of FeBr ₂ in vacuum. Grms.	Weight of Ag in vacuum. Grms.	Loss on fusion. Grm.	Corrected weight of AgBr in vacuum. Grms.	Ratio, FeBr ₂ : 2Ag.	Atomic weight of iron.
6.	3.95460	6.88729	0.00009	6.88720	0.574196	55.831
7.	4.66954	8.13307	0.00025	8.13282	0.574160	55.818
8.	4.75335	8.27870	0.00015	8.27855	0.574177	55.824
9.	6.95582	12.11361	0.00032	12.11329	0.574230	55.844
10.	3.20762	5.58655	0.00023	5.58632	0.574192	55.830
Average					0.574191	55.829
Average, rejecting Nos. 7 and 8					0.574206	55.835

a difference between the two sorts of material lies in the determination of the atomic weight, and since iron is one of the few elements available in sufficient amount for such a comparison, at the close of the research upon the atomic weight of iron described in a previous paper the experiments were continued with meteoric material.

Through the kindness of Prof. John Eliot Wolff, Curator of the Mineralogical Museum of Harvard University, we were fortunate enough to secure a considerable quantity of the "Cumpas" meteorite weighing 63 pounds, found in 1903 near Cumpas, Sonora, Mexico. The meteorite shows well-marked Winmanstättian figures on etching with nitric acid. The sample given us contained a little over 88 per cent of iron, the chief impurity being nickel.

In general, the separation of the iron from the accompanying impurities and the determination of the atomic weight by analysis of ferrous bromide followed the course outlined in the previous paper. The original turnings of meteorite were dissolved in hydrochloric acid, and an insoluble residue which remained was removed by filtration. Upon saturating the solution with hydrogen sulphide, apparently no precipitate except sulphur was formed. The solution was then made nearly neutral by the addition of ammonia, and was again saturated with hydrogen sulphide. The resulting small amount of black precipitate, chiefly ferrous sulphide, was collected upon a filter, and rejected. Next, an excess of ammonia was added, hydrogen sulphide was passed in until precipitation was complete, and the precipitated sulphides were thoroughly washed by decantation. Upon treating the sulphides with 4 per cent hydrochloric acid solution the greater part of the nickel and cobalt sulphides remained insoluble. After filtration the process of precipitating the ferrous sulphide and re-dissolving in dilute hydrochloric acid was repeated. The second residue of nickel and cobalt sulphides was so small that it seemed advisable to remove the remainder of the nickel and cobalt by precipitating the iron as ferric hydroxide in the presence of large amounts of ammonium salts and ammonia. First, the ferrous chloride solution was oxidised by boiling with nitric acid, and then, after dilution, it was poured into a large volume of re-distilled ammonia. The mother-liquor of this precipitation, when evaporated to small bulk and treated with ammonium sulphide, was found to contain nickel; hence the precipitate of ferric hydroxide, after being

washed by decantation, was dissolved in nitric acid and re-precipitated with ammonia as before. In all, nine such precipitations were necessary to eliminate the nickel and cobalt completely. The ninth precipitate of ferric hydroxide was dissolved in re-distilled sulphuric acid, and was converted into ferrous bromide exactly as described in the previous paper with Sample C, by electrolytic reduction and crystallisation as ferrous sulphate, electrolytic deposition as metal from oxalate solution, solution in nitric acid, and crystallisation as ferric nitrate, ignition to oxide, reduction in hydrogen, and solution in concentrated hydrobromic acid solution and crystallisation as ferrous bromide. On account of the limited quantity of material, in the crystallisations of the ferric nitrate and the ferrous bromide the mother-liquors were worked up by the usual process of fractional crystallisation. During the purification of this material no difference in behaviour could be discerned from that of terrestrial iron.

The ferrous bromide was prepared for analysis by dehydration and fusion in a current of dry nitrogen and hydrobromic acid gases, in a quartz boat contained in a quartz tube. After being weighed it was dissolved in acidulated water, and oxidised to the ferric state by dichromate. Finally, the bromine was determined by titration against silver, and the silver bromide was estimated gravimetrically. The details of the procedure were exactly as described in the previous paper. Sufficient material for only five analyses was finally obtained.

While the average of the two series, 55.832, is slightly lower than the outcome of the work described in the previous paper, 55.838, the difference corresponds to only one part in ten thousand in the atomic weight of iron and to less than one part in thirty thousand in the molecular weight of ferrous bromide, the quantity actually determined. It is to be noted that Analyses 4 and 9, in which the largest amount of material was used, gave a result even higher than the average of the preceding series. In the four lowest Analyses, 2 and 7, and 3 and 8, a modification was introduced in the method of analysis, which consisted in adding 98 instead of 99 per cent of the dichromate necessary to oxidise the ferrous salt. In one of these analyses the fused silver bromide, instead of being yellow, was perceptibly darker than the pure substance, possibly owing to slight reduction of the silver salts by the unoxidised

ferrous salt. The ratio of silver to silver bromide in these four experiments is distinctly lower than the value to be expected, 0.574453 (Baxter, *Proc. Am. Acad.*, 1906, xlii., 210; *Journ. Am. Chem. Soc.*, xxviii., 1332).

Analyses 1 and 6	Ag : AgBr.
2 and 7	0.574444
3 and 8	0.574434
4 and 9	0.574436
5 and 10	0.574455
	0.574446

In the previous paper the conclusion was reached that 99 per cent of the dichromate theoretically necessary is sufficient to avoid error from reduction. If the four experiments giving the lowest ratio of silver to silver bromide, 2 and 7 and 3 and 8, are omitted, the averages of the two series become 55.837 and 55.835 respectively, which agree as closely with the final result of the preceding investigation as can be expected. Even the average of the four experiments in question differs from that of the others by only one part in twenty thousand in the molecular weight of ferrous bromide. At any rate, there seems to be no evidence of dissimilarity between this specimen of meteoric iron and the ordinary metal. We intend to investigate this problem further.

We are particularly indebted to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.—*Journal of the American Chemical Society*, xxxiii., No. 3.

COMPRESSIBILITY OF MERCURY.*

By Dr. WM. C. McC. LEWIS.

It has been shown recently that the following expression holds within the limit of error for the majority of normal liquids (*Phil. Mag.*, July, 1911):—

$$L = - \frac{T\alpha}{\rho\beta}$$

where L = the latent heat of vaporisation of the liquid, T = abs. temp., α = coefficient of expansion of the liquid, β = compressibility of the liquid, and ρ = density of the liquid.

In the case of mercury, however, the discrepancy between observed and calculated L is great; and as both L and α are known with considerable accuracy, it seemed likely that the cause of the discrepancy was to be found in the usually accepted value of β . L is calculated from the vapour-pressure data given by M. Knudsen (*Ann. Phys.*, 1909, xxix., 179); the values of α are those given by Callendar and Moss (*Proc. Roy. Soc. A*, 1911, lxxiv., 595, Abstract; cf. *Trans.*, 1911, i.). At 20° C. the calculated value of β is $(1.30 \pm 0.02) \times 10^{-6}$ per kilo/cm². The most recently determined value of β , that of P. Bridgman (*Proc. Amer. Acad.*, 1909, xlv., 255), is 3.70×10^{-6} on the same units. As possible sources of error in experimental determination may be suggested:—

1. Effects produced by a layer of absorbed air or moisture, or both, between the mercury and the walls of the vessel;
2. That the liquid (molasses mixture) into which the piston was dipped before insertion in the mercury is not completely removed; and
3. The unavoidable slip of the mercury past the piston.

All these effects act in the same direction; i.e., they give rise to too great a volume decrease, that is, to too high values of the compressibility.

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

THE USE OF INDICATORS FOR DETERMINING AFFINITY VALUES.*

By V. H. VELEY, F.R.S.

A BRIEF account was given of the use of indicators, especially methyl-orange, for determining the affinity value of acids, as also of bases by the hydrolysis values of their hydrochlorides. The advantages, limitations, and defects of the method proposed were discussed in detail, and especial stress was laid upon the fact that the method, though simple in its execution, is not intended to supersede other methods of greater accuracy, available under like conditions. The data of the hydrolysis, and affinity values deduced therefrom, are independent of the more or less conflicting theories, namely, the ionic and chromophoric, of indicators. Exception was more particularly taken to any correction of the experimental results for the hydrogen ion concentration of the solutions, such correction being based upon theoretical speculations based upon the former theory, which has not met with universal acceptance.

THE ULTRA-VIOLET ABSORPTION SPECTRA OF THE VAPOURS OF VARIOUS ORGANIC SUBSTANCES COMPARED WITH THE ABSORPTION OF THESE SUBSTANCES IN SOLUTION AND IN THIN FILMS.*

By J. E. PURVIS.

Pyridine, α -Picoline, 2:6-Lutidine, 2:4-Lutidine, 2:4:6-Trimethyl Pyridine, and Piperidine.—Pyridine vapour under varying conditions of temperature and pressure shows a considerable number of narrow bands which can be arranged in groups having similar appearances and regular differences in their wave-lengths; α -picoline under similar conditions shows a much less number of bands, but some of them are not unlike those of pyridine. Both these substances also exhibit a strong absorption band in the ultra-violet regions, and more refrangible than the narrow bands. The vapours of the two lutidines and of trimethyl pyridine do not show any narrow bands; but each shows a strong absorption band analogous to that in pyridine and α -picoline. The vapour of piperidine shows a number of bands which can be divided into groups, and which are unlike those of pyridine.

Nicotine, Coniine, and Quinoline.—The vapours of these three substances exhibit none of the series of narrow bands found in the vapour of pyridine. Solutions of nicotine show a band analogous to that of pyridine; solutions of coniine show no band, a result similar to that of piperidine solutions; and quinoline has one large band as vapour, and three solution bands, as first observed by Hartley.

Furan, Furaldehyde, Thiophen, and Pyrrole.—Furan vapour shows some narrow absorption bands; as does the vapour of furaldehyde, but they are different from those of furan; the vapours of thiophen and pyrrole show a few bands, two of which are comparable with two in the vapours of furan and furaldehyde. Solutions of furan, thiophen, and pyrrole show no absorption bands; but solutions of furaldehyde show a strong band in the ultra-violet. Thin films of these three substances show no selective absorption.

Aniline, Mono- and Di-methyl Aniline, Mono- and Di-ethylaniline, o- and m-Toluidine, o-3-Xylidine, m-2-Xylidine, Mesidine, and Benzylamine.—Aniline vapour shows a considerable number of bands which can be divided into similar groups; whilst the vapours of the homologues show none of these narrow bands. In the solutions, the single band of aniline is considerably reduced

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

in persistency when the hydrogen of the amino-group of aniline is replaced by alkyl groups; and when the hydrogen of the nucleus is replaced by alkyl groups, the band becomes large and more persistent.

Chloro- and Bromo-benzenes.—Both vapours show a considerable number of absorption bands, which have general relationships amongst themselves, both in structure and in difference of wave-lengths. Each group of bands in the bromo-benzene vapour is shifted more towards the red end of the spectrum than the corresponding groups of the chloro-benzenes. Solutions of the substances show seven wide diffuse bands which are comparable in appearance, and only differ in position dependent upon differences in the molecular weights. And very thin films exhibit seven wide diffuse bands comparable with the solution bands; they differ in position according to differences of molecular weights.

The author is engaged in a comparative study of the *o*- and *m*-dichloro- and dibromobenzenes, and of *o*- and *m*-chloro and bromotoluenes. The results show that the vapours of these substances have a number of narrow bands, but fewer than those observed in the chloro- and bromobenzenes; and that their solutions and thin films show none of these narrow bands, but that they are replaced by several wide diffuse bands which differ chiefly in their position dependent upon the molecular weights. The orientation in the *o*- and *m*-compounds is also a factor both in the vapours, in the solutions, and in the thin films.

These results may be discussed from a consideration of the movements of the atoms of the molecules being influenced by their nature, weight, type, and orientation. The extent of the free path as well as the impacts of symmetrically and unsymmetrically oriented molecules, and possibly the influence of the radiant energy of the source of light, are also to be considered. The vapour molecules have greater freedom of movement, and a considerable number of bands are produced; unless, as in the case of the pyridine and aniline derivatives, the unsymmetrical orientation of the atoms of the molecules implies a dislocation in the vibrations so that the rhythmical oscillation is destroyed. In solution the solvent acts partly as a constraint on the vibrations, and partly as a barrier to the number of encounters, and partly as an absorbent of the radiant energy, so that the narrow bands of the vapours are usually replaced by wide diffuse bands. In very thin films the movements of the molecules are further restricted as a consequence of the closer packing; but the selective absorption is not unlike that of the solutions; the chief difference being that the bands of the thin films are shifted more towards the less refrangible regions.

ABSORPTION AND DISPERSION IN METALLIC VAPOURS.*

By P. V. BEVAN, M.A., Sc.D.

MORE attention has lately been devoted to the absorption spectra of metals for various reasons. The importance of the subject from the point of view of astrophysics has been more generally recognised, and also the interest of the phenomena from their character as a pure physical or chemical manifestation of the properties of the molecule or atom. Research in these lines has been greatly stimulated by the beautiful results obtained by R. W. Wood in the case of sodium. His observation of forty-eight of the lines of the principal series for sodium was a remarkable extension of our knowledge of series spectra. My own work in this part of the subject has been simply to extend the method of Wood to the other alkali metals, and to find that in the cases of all of them a similar series can be obtained. These series, the first and second members of which are the familiar lines characteristic of the alkali

metals, all appear as absorption lines when white light is passed through the vapours of the metals. With increase of density of the metal more lines come into view, and to obtain a much larger number than have been measured yet requires only greater dispersion in the Spectrograph used. The lines form a series getting closer and closer together at the ultra-violet end of the spectrum, and more powerful instruments are required to resolve more of them. (Slides shown to indicate the character of the spectra). Up to the present I have been able to extend the series to forty-one members in the case of lithium, twenty-four for potassium, thirty for rubidium, and thirty-one for caesium. When it is remembered that in the case of emission spectra only seven members of the series were known for sodium, nine for potassium, five for rubidium, nine for caesium, and nine for lithium, it can be seen what an extension of the field has been made by the new method. Wood has also opened a wide field in the relationship between these absorption spectra and other banded spectra which appear with them and fluorescent and magnetic rotation spectra. The complexity of these spectra is very great, and no more can be said than to refer those who are interested in the matter to Wood's great paper on sodium spectra.

The question of applicability to the series spectra of formulæ based on the work of Rydberg is of great interest. A great deal of work has been done in this region by Hicks and Ritz especially, and formulæ have been proposed which express the series and the relations between different series with the use of surprisingly few constants.

The phenomena of dispersion in metallic vapours is of great interest because of their bearing on optical theory, and on the views we can derive as to the nature of the atom and the vibrating systems that give rise to spectrum lines. Anomalous dispersion has been observed in the cases of all the alkali metals and several others.

I can only refer to the work of Kundt, Becquerel, Ebert, Schön, Puccianti, Lummer, and Pringsheim in this region. The later work of Wood and others has given us a quantitative measure of the effects, and from these we can gain some information as to the nature of atoms. A great deal of work has been done on the dispersion in ordinary gases, but in these cases the region investigated is far from the absorption lines. The case of hydrogen is different, for Ladenburg has shown that when hydrogen is itself excited by an electric discharge it can produce anomalous dispersion effects. This brings it into relation with the alkaline metals, and is strongly in support of the theory that specialised molecules take part in optical phenomena. The difficulty in experiments with metallic vapours is to arrive at absolute measurements, my own work has been concerned with relative measurements at different lines of the principal series. The anomalous dispersion effect takes place at all these lines. Absolute measurements have been made by inference methods by Wood and St. Loria in the case of sodium, and from these, if we know the density of the vapour, we can obtain an estimate of the number of electrons taking part in the effect on light, assuming the dispersion theory of Drude to hold. The fact that Drude's theory gives excellent agreement with experiment for all relative measurements is strong evidence in support of its main correctness. Loria obtained the result from his experiments with sodium vapour at 380° C. that the ratio of the total number of atoms engaged in optical effects to the whole number of atoms was 400 : 3. I calculated from Wood's experiments at 644° C. that the same ratio was about 12 : 1. This depends on a very rough estimate of the density of the vapour, but is of the right order. From measurements at other lines it appears that each line of the series is probably due to a special set of atoms, so that there are indications that the complexity of a spectrum is not due to complexity of each individual atom, but to differences actually existent in the atom. This view has been in the minds of physicists for some time, and there is hope that work on the lines described may enable us to find out something of the nature of the differences. A good deal of evidence of other kinds leads in

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

the same direction—the Zeeman effect, the magnetic rotation of the plane of polarisation, and so on; but this is not the occasion to discuss these problems.

An interesting method of preparing rubidium and caesium may be mentioned. Hackspill found they could be prepared by heating the chlorides with calcium. I found in some early experiments that the metals could be obtained by heating the chlorides with sodium, and later that if lithium be used the vapours are obtained practically pure owing to the much greater temperature required for vaporising lithium than for the other metals.

SOME POINTS CONCERNING THE TREATMENT OF WHEATEN FLOUR.*

By A. E. HUMPHRIES.

AT the Leicester and Winnipeg meetings of this Association the author dealt with some phases of the complex questions concerning the quality of wheaten flour. Great importance must be attached to "strength," a flour's capacity for making big, shapely, and therefore well-aerated loaves. The nice appearance of food is a factor affecting its dietetic value. The whiteness of bread depends to a very great extent upon the "strength" of the flour used, for the good appearance of bread depends very largely on the perfect aëration of the loaf. "Strength" does not depend upon any one factor. A flour with a high protein-content is not necessarily strong. A flour with a low protein-content is probably, but not necessarily, weak.

The size of the loaf depends upon the production of sufficient gas during fermentation, more particularly during the later stages, and upon the gas-retaining capacity of the dough. The yeast must have a sufficiency of sugar, nitrogenous and mineral foods in forms which it can assimilate. Flour itself does not contain sufficient sugar for the requirements of the yeast. As a general proposition it is true to say that flour made from wheats harvested in moist atmospheric conditions yield as a result of diastatic action during panary fermentation a sufficient quantity of sugar, those harvested in hot dry conditions do not. The yeast requires its nitrogenous food in a very simple form. Flours containing a very high percentage of nitrogenous matter do not necessarily provide a sufficiency of nitrogenous yeast-food. It is believed that yeast can obtain all the mineral matter it requires from flour, but there are cases in which the addition of mineral phosphates does increase the yield of gas in panary fermentation conducted under commercial conditions. A flour may possess a high percentage of gluten, but unless it yields in fermentation sufficient gas to overcome the great and variable leak, and thoroughly to inflate the dough in the latest stages of the breadmaking process, it would be accounted weak.

Furthermore, a flour may yield more than sufficient gas at all stages of fermentation and may even possess a high percentage of nitrogenous matter and yet produce very small loaves. Dr. Hardy at the Winnipeg meeting of this Association showed that gluten loses its tenacity and ductility if it be deprived of its electrolytes. Prof. T. B. Wood has demonstrated the profound influence which very dilute solutions of acids, alkalis, and salts have on the physical characteristics of gluten. It has been found that additions of very small percentages of salts natural to flour or wheaten ash do increase the size of the loaf even though the production of gas in fermentation be unaffected or actually diminished.

The author came across a case in which the mere addition of water, if made at a time substantially prior to dough making, increased the strength of the flour to an extraordinary extent even though the yield of gas in fermentation was not appreciably increased thereby.

He therefore, with the assistance of his colleague, Mr. A. G. Simpson, made an investigation of the changes produced, the results of which were set forth in detail. The most striking change in the flour itself appears to be the transformation of organic phosphorus compounds into inorganic. As part of these investigations, it has been found that during the process of baking a large proportion of the organic phosphorus compounds becomes inorganic.

British millers nowadays obtain their raw material from all parts of the world, a multitude of varieties raised in environments ranging from arctic or semi-arctic to tropical or semi-tropical. The climatic conditions in most districts also vary greatly from season to season. From such extremely diverse and variable materials, they have to produce flours of uniform qualities. It is therefore right and proper that they should be allowed to make use of the advances in chemical knowledge in the treatment of wheats and flours. Sometimes the desirable treatment can be limited to the adjustment of water content, Nature herself being thereby enabled to effect the necessary changes.

Sometimes the addition of water fails to bring about these changes, or for various reasons it is undesirable to raise the water content sufficiently, and in such cases the addition of diastatic bodies, nitrogenous yeast-foods, and salts natural to wheat or wheaten ash is desirable and should be permitted. But inasmuch as such permission might be abused, a Board of Reference consisting of highly qualified physiologists, chemists, and business men should be established, to whom all such processes and additions should be submitted, and to whom millers and bakers should be responsible in such matters.

OBITUARY.

DR. ALBERT LADENBURG.

WE regret to announce that the death of Dr. Albert Ladenburg, Ph.D., Hon.M.D., Professor of Chemistry at University of Breslau, has recently taken place after a long illness.

Dr. Ladenburg was born at Mannheim on July 2nd, 1842, and studied at Heidelberg, where he graduated as Doctor of Philosophy in 1863. After some time spent in teaching at Heidelberg he obtained the post of Professor of Chemistry at the University of Kiel, and in 1890 he was called to the Chair of Chemistry at Breslau.

Dr. Ladenburg's researches lay chiefly in the region of organic chemistry, which he enriched by many important discoveries. His best known researches were possibly those on the metameric relations of the benzene derivatives, and his work on terephthalic acid contributed largely to the elucidation of the structure of the ortho-, meta-, and para-compounds. He also investigated the pyridine bases, and his admirable experimental work on them brought to light the connection between pyridine and piperidine, while by his method of reducing the pyridine bases by means of sodium many important compounds have been obtained and their structure proved. Thus, cadaverine has been prepared from trimethylene cyanide. By the application of the same method Ladenburg effected the synthesis of coniine, one of the most brilliant of his achievements. He also prepared and investigated many organic derivatives of silicon, and by his excellent quantitative work proved conclusively that the molecule of ozone consists of three atoms of oxygen.

Dr. Ladenburg showed considerable literary activity, and his "Vorträge über die Entwicklungsgeschichte der Chemie in den letzten 100 Jahren," first published in 1869, is a valuable work on the history of chemistry. He was the editor of the chemical section of the "Encyclopädie der Naturwissenschaften," which was issued in thirteen volumes under the title of "Handwörterbuch der Chemie." He was a most successful and stimulating teacher, and the whole scientific world has suffered a severe loss by his death.

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

NOTICES OF BOOKS.

Über Katalyse. ("Catalysis"). By WILHELM OSTWALD. Second Edition. Leipzig: Akademische Verlagsgesellschaft m.b.H. 1911. (1 Mk. 50).

THIS pamphlet contains the lecture delivered on December 12, 1909, in the theatre of the Swedish Academy of Sciences by Prof. Ostwald on the occasion of his recommendation for the Nobel Prize for Chemistry. He took as his subject catalysis, and gave a very interesting account of the growth of our knowledge of catalysers and catalytic reactions—a growth which may be very largely ascribed to his own work and the inspiration he has given to others. Allusions were made in the lecture to the researches of the chemists who paved the way for modern investigators, and an outline of recent work was sketched, while the lecturer indicated the lines of research which he would expect to lead to the complete successful solution of the problem of the true nature of catalysis.

Allgemeine Chemie der Enzyme. ("General Chemistry of the Enzymes"). By HANS EULER. Wiesbaden: J. F. Bergmann. 1910. (5 M. 70).

ALTHOUGH it may in one sense be true that our knowledge of enzyme chemistry is as yet very scanty, full of gaps, and even of errors, there is much to be said for the author's contention that the time is ripe for the appearance of a short *résumé*, collecting and criticising the data which have been accumulated. Methods of investigation have recently been much improved, and more careful study has elucidated the mechanism of some of the reactions involved, while reliable quantitative results have been obtained. This book, which treats of the chemistry, general and physical, of the enzymes, will be of service both to scientific men who are engaged in enzymological research, and to those whose work lies more in the region of the practical applications of the science. The subject is very systematically treated and well subdivided. After a section on the preparation and properties of the individual enzymes, the general physical properties of the substances are discussed and then the chemical dynamics of enzyme reactions are considered, with the experimental results which have been obtained in the study of the course of the reactions. A brief outline is given of the results of the investigation of the influence of temperature and of different radiations on enzymatological actions and the syntheses which enzymes can effect are summarised.

CORRESPONDENCE.

CURIOUS THERMAL PHENOMENON.

To the Editor of the Chemical News.

SIR,—With regard to the anomalous increase of temperature observable in a portion of a heated bar or plate when the other portion is suddenly cooled, about which I recently wrote (CHEMICAL NEWS, civ., 96), I have devised a more satisfactory method for testing the accuracy of the observation, which I now append.

A rod or bar of metal 10 inches or more in length is coated *very thinly* with wax, a mere film will do, and then brushed over lightly with red mercuric iodide. A number of fine parallel scratches can be made through this layer to serve as reference marks. If one end of the rod is now heated, the gradual rise of temperature can be easily followed by watching the change of colour from red to yellow, a change which is very sharp and distinct. When the bar has been suitably heated, the flame is removed, and the change from red to yellow allowed to attain its maximum extension (this will take a variable time, of

course, according to the thickness and material of the rod). When no further change takes place, immerse the bar gradually in cold water, starting from the hot end and finishing near the transition line of colour, and it will be found that usually there is a distinct rise of temperature in the uncooled portion, shown by a slight extension of the zone of yellow iodide.

Can there be oscillations of temperature in such a bar, due to the sudden shrinking of the cooled particles exciting a wave of more or less violent molecular vibrations to travel along the bar, and thus raise the temperature of parts not too remote from the scene of the disturbance. In trying the above mentioned experiment many times over, it has seemed always as if the results were more distinct when a gradual (but not too slow) cooling was caused than when the bar was plunged in suddenly to the limiting point. This, if correct, would show that the effect was of a cumulative nature, that the wave required a certain time to gather its maximum effect. It would follow that different rates of cooling would produce maximum effects in rods of different materials, owing to differences of conductivity, &c., but I have not been able to test this; thermo-electric measurements would undoubtedly be the most suitable means of investigating the whole matter, but I have no such appliances here.—I am, &c.,

E. G. BRYANT.

Grey Institute, Port Elizabeth,
August 6, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

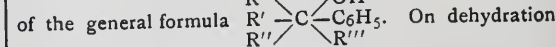
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 25, June 19, 1911.

Allotropic Modifications and Melting-point of Arsenic.—Pierre Jolibois.—By studying the thermic phenomena which are produced when arsenic is heated and cooled in different conditions the author has endeavoured to obtain fresh proofs of the existence of the allotropic modifications of the element. He finds that grey arsenic is stable at all temperatures up to 850°. Glittering arsenic is unstable at all temperatures, and is transformed into grey arsenic at about 280° by an irreversible reaction. The melting-point of grey arsenic, determined by two different methods is 850° ± 10°.

Action of Syrupy Phosphoric Acid on Alloys obtained in an Electric Furnace.—Max Wunder and B. Jeanneret.—Syrupy phosphoric acid attacks the following metals or alloys with more or less ease:—Si, Zr, W, ferro-silicon, ferro-titanium, ferro-zirconium, ferro-vanadium, silico-manganese, titanium nitride, alloy of iron, silicon and aluminium, boro-nickel, carborundum. The carbon contained in the alloys remains, either wholly or in part, in a flaky state in the syrupy liquid.

Dehydration of Alkyl and Benzylpseudobutylphenyl Carbinols.—Pauline Lucas.—The action of organo-magnesium derivatives on trialkylacetophenones gives alcohols of the general formula



On dehydration these yield hydrocarbons. In the case of methylpseudobutylphenyl carbinol the hydrocarbon obtained is a mixture of 2-phenyl-3,3-dimethyl-1-butene and 1-phenyl-2,2-dimethylcyclopropane. From ethylpseudobutylphenyl carbinol only 3-phenyl-4,4-dimethyl-2-pentene is obtained, and from pseudobutylbenzylphenyl carbinol 1,2-diphenyl-3,3-dimethyl-1-butene.

a-Glucose and Glucose.—L. H. Philippe.—When nascent hydrogen acts on a-glucoseconic acid the

latter is transformed into α -glucose, and then into the corresponding alcohol glucoside. The melting-point of the decose is 210° , and in 10 per cent solution its initial rotatory power is about $+37^\circ$. When sodium amalgam acts on the decose, first in acid and then in neutral solution, it yields the decite, the melting-point of which is 222° ; its rotatory power is $[\alpha]_{18} = +1.2^\circ$.

Bulletin de la Société Chimique de France.
Vol. ix.-x., No. 11, 1911.

Extraction of Bromine and Iodine by Chloroform and Carbon Disulphide.—A. Labat.—The investigation of methods of determining the halogens in a mixture of aqueous solutions of alkaline iodides and bromides shows that when setting them free by an oxidising agent and a solvent such as chloroform and carbon disulphide, it is best to avoid the use of chlorine because some iodine may be lost. Sodium nitrite is only useful for iodine alone.

Preparation of Nitrides by Reduction of Alkaline Cyanides.—A. C. Vournasos.—Boron, aluminium, cerium, and lanthanum exercise a reducing action on alkaline cyanides, nitrides being formed. Thus boron nitride can be obtained as a white powder, decomposed with difficulty by water, while aluminium nitride is an amorphous yellowish powder, which is easily decomposed by alkalis and mineral acids. The nitrides of cerium and lanthanum are amorphous white powders, which give ammonia with warm water.

Formula of Uranium Carbide.—Paul Lebeau.—The analysis of melts of uranium and carbon, and metallographic examination show that the formula C_2U_3 cannot be correct, and the author's analytical results give C_2U as the formula. Thus the carbide of uranium resembles the carbides of the rare earths both as regards its formula and its properties. It is most like thorium carbide in the complexity of the products of its decomposition with water.

Hydrogenation by Precipitated Palladium and Sodium Hypophosphite.—Pierre Breteau.—Palladium can be precipitated from a solution of its chloride by means of sodium hypophosphite, either in a neutral acid or alkaline medium, and the palladium thus obtained can oxidise an unlimited amount of hypophosphite in the cold. The hydrogen thus set free readily hydrogenates phenanthrene, giving the tetrahydride. By the same method nitro and dinitro derivatives can be transformed into amines.

Hydrogenation by means of Nickel and Sodium Hypophosphite.—Pierre Breteau.—Nickel can be precipitated from its sulphate by the addition of sodium hypophosphite. The nickel powder thus obtained readily decomposes water in presence of sodium hypophosphite, but the hydrogen set free will not hydrogenate phenanthrene.

Basic Properties of the Oxygen of Ethers.—D. E. Tsakalotos.—The author has studied the two systems acetic acid-ethyl ether and trichloroacetic acid-ethyl ether in order to determine the conditions in which the ethers can combine with the acids. From determinations of the coefficients of viscosity and density it appears that the ethers behave like feeble bases. They form molecular compounds with strong acids (HCl, HBr, CCl_3COOH), but do not combine with feeble acids like acetic acid.

Decomposition by Heat of Metallic Xanthates.—Alexandre Hébert.—The xanthates of Ba, Fe, Co, Ni, Zn, Cu, Pb, Hg, Ag, Sn can readily be prepared by double decompositions. When they are subjected to distillation at 350° gases are evolved, consisting of H_2S , CO_2 , and combustible gases in varying proportions. The way in which the xanthates decompose seems to bear no relation to the properties of the metals they contain. Thus the salts of K, Ba, Fe, Co, Zn, Pb, Sn give practically the same kind of gaseous liquid and solid products, while those of Ni, Cu, Hg, and Ag give chiefly ethylxanthate of ethyl.

Salts and Ethers of Alkylamino-dithiocarbonic Acids.—E. Fourneau.—The dithiocarbonate derived from methylaminoacetic acid can be prepared by adding carbon disulphide to an ethereal solution of methylaminoacetate of ethyl, and re-crystallising. The addition of mercuric chloride gives the methylaminoacetate of ethyl dithiocarbonate of mercury. The author has prepared this and similar compounds, and investigated their properties.

Phenoxthine.—E. Ferrario.—In presence of a catalyser, such as anhydrous magnesium chloride or aluminium chloride, phenoxthine can be prepared by making sulphur react with phenyl oxide. When phenoxthine is reduced, two atoms of hydrogen are added on. When it is treated with metallic copper at 250° it gives a good yield of diphenylene oxide.

Modification of Malaquin's Reaction for the Characterisation of Strychnine.—G. Denigès.—Malaquin detected strychnine by adding zinc and hydrochloric acid to the solution to be tested, and after a few minutes adding concentrated sulphuric acid, when a pink ring is formed where the two liquids meet if strychnine is present. The test sometimes fails, especially if the zinc used is not previously washed with nitric acid. Apparently strychnine yields tetrahydrostrychnine, mixed with more or less of its anhydride strychnidine. Both products are attacked by oxidising agents giving pink colorations. In order to render the test more reliable it is only necessary not to wash the zinc in nitric acid, but to add a drop of KNO_3 or $NaNO_3$ to the strychnine solution.

New Characteristic Reaction of Bromine.—G. Denigès.—Bromine gives a purple coloration with a characteristic absorption spectrum if an aqueous solution, containing not more than 1 gm. per litre, is added to a solution containing 5 cc. of a 1 per cent solution of strychnine, 5 cc. of pure hydrochloric acid, and 4 or 5 grms. of zinc amalgam or chemically pure zinc.

Rapid Method of Determining Nitrates and Nitrites in Water.—G. Denigès.—The strychnine reagent mentioned in the previous paper can be used to detect nitrates and nitrites in water. If nitrites are present 10 cc. of the water gives a pink tinge if 0.5 cc. of the solution is added to it. The amount of nitrite can be estimated colorimetrically. If nitrates are present and no nitrites, no reaction occurs unless half its volume of sulphuric acid is added to the liquid, when the coloration appears. If both nitrites and nitrates are present the former can be determined first, and then the effect of adding sulphuric acid observed.

Negative Case of Indigoid Condensation.—E. Pisoschi.—The author obtained 6-nitro-veratric aldehyde by methylating vanillin, and nitrating the veratric aldehyde thus prepared. This compound, which is a derivative of o-nitrobenzaldehyde, should react with acetone in presence of an alkali to give 5-6-5'-6'-tetramethoxyindigo, but the author has never succeeded in obtaining the reaction in spite of many variations in the experimental conditions.

Properties of different Varieties of Dammar Resin.—Ch. Coffignier.—Under the general name Dammar many different varieties of resin are included. In this paper the author gives the results of the examination of the solubilities of many varieties, using various solvents.

Zeitschrift für Anorganische Chemie.
Vol. lxxi., No. 1, 1911.

Formation of Conversion Saltpetre from the Point of View of the Phase Law.—Ernst Jänecke.—In this paper the author gives examples of his new method of graphically reproducing the solubility proportions of reciprocal pairs of salts, namely, $NaCl-KNO_3$, $KCl-NaNO_3$ at 25° , and $NaNO_3-K_2CO_3$, $KNO_3-Na_2CO_3$ at 10° and 24.2° . He also describes a new method of graphic representation, by means of which it is possible to deduce

directly the relations between percentages by weight and molecular percentages.

Detection and Determination of Thorium with Iodic Acid.—R. J. Meyer.—Iodic acid is an absolutely reliable reagent for determining small amounts of thorium. The solution must contain nitric acid, and a large excess of the precipitating reagent must be employed. Two solutions are required, a concentrated solution containing 15 grms. KIO_3 , 50 cc. conc. HNO_3 , and 100 cc. water, and a dilute solution, containing 4 grms. KIO_3 , 100 cc. dil. HNO_3 , and 400 cc. water. Five cc. of solution I. are added to 2 cc. of the solution to be tested, and then 10 cc. of solution II. On boiling the thorium iodate precipitated remains undissolved, while the iodates of the cerite and yttrium earths go into solution. Zirconium gives the same reaction as thorium, but zirconium iodate is soluble in oxalic acid, while thorium iodate is not. Hence if zirconium is present the precipitate must be washed with oxalic acid. The iodic acid can be used to separate thorium quantitatively from scandium.

Hydratisation of Metaphosphoric Acid.—D. Balareff.—From the results obtained in the study of the hydratisation of metaphosphoric acid in a Schuller-Warthe's ice calorimeter it is found that Thomsen's thermochemical method of investigation is not applicable to the solution of this problem, owing to the thermic effects produced when the aqueous solutions of ortho and metaphosphoric acids are mixed.

Hydrates of Arsenic Pentoxide.—D. Balareff.—On evaporating a solution of arsenic acid both at 180° and 40° , $\text{H}_5\text{As}_3\text{O}_{10}$ separates out. From solutions of different concentrations at the ordinary temperature on cooling, $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ or a mixture of $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{H}_5\text{As}_3\text{O}_{10}$ separates out. When $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is dried $\text{H}_5\text{As}_3\text{O}_{10}$ is formed, and when it is heated it decomposes into $\text{H}_5\text{As}_3\text{O}_{10}$ and an aqueous solution.

Thallous Hydroxide.—Fritz Bahr.—Saturated solutions of thallous hydroxide can be prepared by passing pure oxygen over metallic thorium and water, and shaking thoroughly, and the pure hydroxide can be made to separate out in the solid crystalline state. The dissociation point of thallous hydroxide is 139° . Thallous hydroxide is sensitive to light, but it has not been determined what chemical reaction occurs.

Atti della Reale Accademia des Lincei.

Vol. xx., No. 9, 1911.

Formation of Metallic Solid Solutions by Diffusion in the Solid State.—G. Bruni and D. Meneghini.—By covering a nickel wire with copper and determining the electrical resistance, the authors have shown that the two metals which form solid solutions in all proportions also give them by diffusing, one into the other, in the solid state.

Preparation and Phototropism of some Osazones.—M. Padoa and L. Santi.—The authors have prepared many osazones, and have studied the effect of light upon them. They find that the β -m-tolyllosazone of benzoyl is feebly phototropic; the corresponding osazones of phenyl and anisyl are both phototropic, as are also the β -naphthyllosazone and the β -tolyllosazone of anisyl.

Vol. xx., No. 10, 1911.

Binary System CuBr—KBr.—P. de Cesaris.—The author has determined the fusion-point curve of mixtures of copper bromide and potassium bromide. In mixtures containing from 95 to 5 per cent CuBr there is always a eutectic point at 182° .

Thermic Analysis of Binary Mixtures of Chlorides of Monovalent Metals.—Carlo Sandonnini.—When the chlorides of sodium and silver are fused together they deposit mixed crystals of the same form in all proportions. Lithium and silver chlorides give mixed crystals of two kinds. There is a break in the miscibility between 16 and

50 molecules per cent AgCl. Lithium chloride and cuprous chloride give pure mixed crystals of two species. There is a break in the miscibility from about 25 to 55 molecules per cent CuCl. The solidification curve exhibits a minimum.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Portsmouth Meeting of the British Association:—

President—Prof. J. Walker, D.Sc., F.R.S.

Vice-Presidents—J. E. Stead, F.R.S.; Prof. A. Béhal; Prof. A. Haller; Prof. W. J. Pope, F.R.S.; Prof. A. Senior, M.D., Ph.D.

Secretaries—E. F. Armstrong, D.Sc. (Recorder); C. H. Desch, D.Sc.; T. M. Lowry, D.Sc.; F. Beddow, D.Sc.

Committee—Dr. G. Barger; Dr. H. Bassett, jun.; Prof. C. Barus; Dr. A. C. Cumming; Prof. E. Divers, F.R.S.; Prof. H. B. Dixon, F.R.S.; Prof. H. Euler; Dr. A. Findlay; Prof. H. Freundlich; Dr. R. W. Gray; Mr. Vernon Harcourt, F.R.S.; Dr. A. Holt; Dr. W. C. Lewis; Prof. H. Marshall, F.R.S.; Dr. R. S. Morell; Prof. A. A. Noyes; Prof. K. J. P. Orton; Dr. H. Ramage; Prof. Sir W. Ramsay, K.C.B., F.R.S.; Prof. Emerson Reynolds, F.R.S.; Dr. H. J. Sand; Dr. I. Smedley; Dr. S. Smiles; Prof. Smithells, F.R.S.; Dr. J. F. Thorpe, F.R.S.; Mr. H. T. Tizard; Dr. A. E. Tutton, F.R.S.; Prof. R. Wegscheider; Dr. N. T. M. Wilsmore.

The Papers brought before the Section were as follows:—

- Prof. J. WALKER, F.R.S.—Presidential Address.
- Prof. C. BARUS—Diffusion of Gases through Water.
- Prof. A. McWILLIAM—Electric Steel Furnaces.
- Dr. W. C. LEWIS—Compressibility of Mercury.
- Dr. J. F. THORPE—Chemistry of the Glutamic Acids.
- G. LE BAS—Influence of Constitution on the Molecular Volumes of Organic Compounds at the Boiling-point.
- Prof. R. WEGSCHEIDER—Influence of Substituents on Reaction Velocities.
- Report of the Committee on the Influence of Carbon and other Elements on the Corrosion of Steel.
- Dr. V. H. VELEY—Application of Methyl-orange for the Determination of the Affinity Constants of Weak Acids and Bases, with a Discussion of the Errors.
- H. T. TIZARD—Sensitiveness of Indicators.
- Dr. T. M. LOWRY—Origin of General and of Specific Absorption.
- J. E. PURVIS—Absorption Spectra of Vapours.
- P. V. BEVAN—Absorption Spectra and Refractive Power of Metallic Vapours.
- Prof. W. H. PERKIN and W. J. POPE—Optically Active Systems containing no Asymmetric Atom.
- Report of the Committee on the Study of Isomorphous Sulphonic Derivatives of Benzene.
- Discussion on the Part Played by Enzymes in the Economy of Plants and Animals, opened by Dr. E. F. ARMSTRONG.
- Prof. H. EULER—Velocity of Formation of Enzyme Systems.
- A. E. HUMPHRIES—Some Points concerning the Treatment of Wheat Flour.
- Prof. FREUNDLICH—Theory of Colloids.
- Dr. G. BARGER—Colloids in Pharmacy.
- Dr. G. BARGER—Blue Adsorption Compounds of Iodine with Starch and other Substances.
- Dr. C. H. DESCH—Colloid Theory of Cements.
- H. H. PAINE—Rate of Coagulation of Colloidal Copper.
- Report of Committee on the Study of Hydroaromatic Substances.
- Report of Committee on the Transformation of Aromatic Nitroamines.
- Report of Committee on Electro-analysis.

THE CHEMICAL NEWS.

VOL. CIV., No. 2703.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate is admitted to this Examination unless he has passed, or been admitted under the Statute referred to above as exempt from, a Matriculation Examination not later than that of the preceding January.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lees Reader in Chemistry—H. Brereton Baker, M.A., D.Sc., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: Dr. Baker, A. L. Parson, B.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. *Jesus College Laboratory*: D. L. Chapman, M.A. *Queen's College Laboratory*: Rev. G. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University, either by examination or by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is

published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

Junior Demonstrator—H. Krall, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry*.—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(UNIVERSITY OF LONDON).

Senior Professor of Chemistry—J. M. Thomson, LL.D. F.R.S.

Professors—Herbert Jackson, F.C.S., and P. H. Kirkaldy, F.C.S.

Lecturer and Demonstrators—H. L. Smith, B.Sc., S. W. Collins, B.Sc. and L. E. Hinkel.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1911-1912 are Oct. 4, Jan. 10, and May 1.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the

laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visà voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s. Practical Chemistry: Winter Session, £5 8s.; Summer Session, £4 4s.; or £10 10s per annum. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; One Term, £10 10s.; Two Terms, £18 18s.; Three Terms, £26 5s. Three days a week: One month, £2 12s. 6d.; One Term, £6 6s.; Two Terms, £11 11s.; Three Terms, £15 15s.

For fuller details the separate Syllabuses provided for each class should be consulted.

METALLURGY.

Professor—A. K. Huntington, A.R.S.M., F.I.C., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course. (For full details apply to Prof. Huntington).

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, LL.D., F.R.S.

For particulars apply to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

(UNIVERSITY OF LONDON).

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. Inorganic and Physical Chemistry; J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—R. W. Gray, Ph.D.; J. Sniles D.Sc.; N. T. M. Wismore, M.Sc.; Katharine A. Burke, B.Sc.; W. C. McC. Lewis D.Sc.; W. B. Tuck, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 2 to December 20; Second Term, from January 9 to March 29; Third Term, from April 30 to June 10.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c.; borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees: Course, £7 7s.; First or Second Terms, £4 4s. A Practical Class will meet throughout the Session.

Courses of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to July: Tuesday and Thursday at 9.

The Courses comprise Stoichiometry, the Liquid and Solid States of Matter, the Phase Rule, Thermochemistry, and in general the Application of Physical Methods to the Solution of Chemical Problems, Chemical Statics, the Electrolytic Dissociation Theory, Chemical Dynamics, and Chemical Thermodynamics.

Fees:—Courses, £5 5s.; Term, £2 2s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professor—Sir W. A. Tilden, D.Sc., F.R.S.

Professor and Director of the Chemical Laboratories—Sir T. E. Thorpe, C.B., F.R.S., &c.

Assistant Professors—M. O. Foster, P.I.D., D.Sc., F.R.S.; G. T. Morgan, D.Sc., A.R.C.S.; J. C. Philip, M.A., Ph.D., B.Sc.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

Subject to agreement with the authorities of any College or other Institution, the Governing Body may by resolution recognise that College or Institution or any Department thereof, as being in association with the Imperial College for all or any of the purposes of the Charter, but no such resolution is to be valid or operative until allowed by the King in Council.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute (A.C.G.I.) in one or more of the following divisions:—Chemistry, Engineering (Civil and Mechanical), Engineering (Electrical).

The instruction in Chemical Science embraces:—

1. Courses of lectures on the laws and general principles of Chemistry, including the special study of compounds of carbon, usually called "Organic Chemistry"; on the theory and methods of Chemical Analysis; and on Physical Chemistry.

2. A systematic Laboratory course for the practice of Qualitative and Quantitative Analysis.

An examination will be held at the end of each course of instruction, and all candidates for a Diploma in Chemistry will be required to qualify in each successive stage.

A Laboratory course is provided for advanced students desirous of acquiring a knowledge of the methods employed in research and for the prosecution of Chemical Investigations.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The 70th Session will commence on Oct. 4, 1911.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S. (Dean); Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy is also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Director of the Edward Davies Chemical Laboratories and Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, M.A. (Cantab.), B.Sc. *Student Assistant*—Miss M. K. Turner, B.Sc. (Lond.).

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 3rd, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1910-1911, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their second year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 6 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student

to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 19, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. *Assistant Lecturer and Demonstrator*, Alice E. Smith, B.Sc. *Lecturer in Agricultural Chemistry*, H. E. Jones, B.A., B.Sc. *Junior Demonstrator*, J. O. Hughes, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. *Assistant Lecturers and Demonstrators*, A. H. Ferguson, B.Sc., and W. E. Williams, B.Sc.

The Session opens October 3rd, 1911. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s. Advanced Lectures on Organic Chemistry, £1 1s. *Agricultural Chemistry*.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.

Professor in Metallurgy—A. A. Read, M.Met., F.I.C., F.C.S.

The Session commences October 3rd, and terminates on June 28th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 4s.

The Senior Course consists of about 50 lectures on Organic Chemistry; Fee, £3 3s.

A course on Inorganic Chemistry will be given in the Session 1912-1913.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

DEPARTMENT OF CHEMISTRY.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., F.I.C.; F. W. Rixon, M.Sc., Ph.D.

Lecturer in Inorganic and Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Agricultural Chemistry—C. T. Gillingham, F.I.C.

Lecturer in Hygienic Chemistry—F. Wallis Stoddart, F.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1911-1912 commences on October 3, and ends on July 1, 1912.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 ampères from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electro-metallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and

manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

DAY LECTURES.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work. 3. Physical Chemistry—Two Lectures per week for two Sessions and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—*Intermediate Science*—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following Special Courses as directed, e.g.:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio-chemistry.

The Colloquium and meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.

2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.

3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

EVENING LECTURES.

The Laboratories are opened from 6.30 to 9.30 p.m. on Tuesday during the Autumn and Spring Terms. Course 1 will be given on Wednesday at 8 to 9, and Course 2 or 3 on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course 1 will be similar to that given to Intermediate Students in the Faculty of Science, and that given in Course 2 or 3 to one of those given to Students studying for the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.

2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical

teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articulated pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.
Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.
Demonstrators—A. C. Higgs and E. G. Moody.
Assistant in Chemical Laboratory—H. Thwaites.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught at the University College. The Engineering work of the University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, October 2nd.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators—Alex. Findlay, M.A., D.Sc., Ph.D.; Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, D.Sc., and T. J. Murray, Ph.D., M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 2nd, 1911.

The Chemical Department is now housed in the new University buildings at Bournbrook.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—*Advanced Organic Chemistry.*—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £1 11s. 6d.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General, Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. GARDNER, M.Sc.

DEPARTMENT OF CHEMISTRY AND DYEING.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc.

Assistant Professor of Chemistry—B. North, A.R.C.S. (Lond.).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. H. Hodgson, M.A., B.Sc., Ph.D.; S. F. Stell, F.C.S.

Demonstrators in Chemistry—M. Fort, B.Sc.; S. M. Sutcliffe, F.C.S.

Lecturer in Physics—J. A. Tomkins, A.R.C.S. (Lond.).

Demonstrator in Physics—F. Harcourt, B.Sc.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Demonstrator in Dyeing—T. Brooke.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Past Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. A completely equipped Practical Dyehouse and Finishing Rooms have now been added.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Special Courses for Graduates in Chemistry, and for Drysalers, Colour Merchants, &c.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board* (M.R.C.S., L.R.C.P.), London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Demonstrator—M. Kershaw, B.A., Ag.Dip. Cambs.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Assistant Lecturers and Demonstrators—W. Lowson, B.Sc., F.I.C.; W. H. Perkins, B.Sc.

Demonstrators—H. Calam, M.Sc.; J. Marshall, B.Sc.; H. S. Patterson, B.Sc.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.

2. Advanced Inorganic Chemistry.—(A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.

3. Advanced Inorganic Chemistry.—(B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon Fee, £4 10s.

5. Honours Courses.—(a) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £3 7s. 6d. (b) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First

Term; fee, £2 5s. (c) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £3 7s. 6d. (d) Electro-chemistry: One hour weekly; £2 10s.

6. Chemistry of Food and Drugs—Special class for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—£3 per half day of three hours per week.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—G. H. Frank, M.Sc.

Demonstrator—A. Woodhead, M.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Professor—E. Stiasny, Ph.D.

Demonstrator—Harold Brumwell.

Research Assistant—A. Seymour-Jones, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture at the University Farm.

Fuel and Metallurgical Department.

Professor—William A. Bone, D.Sc., Ph.D., F.R.S.

Demonstrator and Research Assistant—H. H. Gray, B.Sc.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the micro-structure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City

Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, F.R.S.

Professor of Physical Chemistry—F. G. Donnan, M.A.

Ph.D.

Professor of Bio-chemistry—Benjamin Moore, M.A., D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—Guy D. Bengough, M.A., A.R.S.M.

Assistant Lecturers and Demonstrators—H. Bassett, D.Sc., Ph.D., Francis W. Kay, M.Sc., Ph.D.; A. Rule, M.Sc., Ph.D.; R. E. Slade, M.Sc.; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froyssell.

The Session commences October 4th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic, Physical, and Bio-chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Course J.—Applied Inorganic Chemistry, including Metallurgy. Fee, £2.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L.—Applied Electro-chemistry. Fee, £2 10s.

Also Pass and Honours Courses in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1911, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE. (IN THE UNIVERSITY OF DURHAM).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturer and Demonstrator—A. A. Hall, M.Sc., Ph.D.

Demonstrator—J. H. Paterson, B.Sc.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant to Lecturer in Agricultural Chemistry—E. F. Taylor, B.Sc.

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 3rd. The class for Inorganic Chemistry meets at 3 p.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

Applied Chemistry.—Tuesday, 5—6 p.m. Lectures on Fuel, Gas Analysis, Technology of Acid and Alkali. Fee, £3 10s. per Session.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc.,

A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(a) Religious Knowledge, (b) Latin, (c) Greek, (d) French, (e) German, (f) some other language to be approved, (g) Experimental Science or Physics or Chemistry, (h) Botany or Zoology, (i) Mechanics, (k) Extra Mathematics, (l) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iii.). Foreign Students may be exempted from the Matriculation Examination on report from the Board of Professors of Armstrong College, that they have already passed an examination equivalent to the Matriculation Examination of the University, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, September 29th, 1910. Candidates

should send in their names to the Secretary on or before September 11th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing October 3rd. Candidates should send in their names to the Secretary on or before September 24th.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Inorganic Laboratories.—Harold B. Dixon, M.A., M.Sc., Ph.D., F.R.S.

Professor of Chemistry and Director of the Organic Laboratories.—W. H. Perkin, Ph.D., D.Sc., F.R.S.

Senior Lecturers and Demonstrators.—Arthur Lapworth, D.Sc., F.R.S.; C. Weizmann, Ph.D., D.Sc.; Norman Smith, D.Sc.; and E. C. Edgar, D.Sc.

Assistant Lecturers and Demonstrators.—Robert Robinson, D.Sc.; A. Holt, M.A., D.Sc.; F. P. Burt, B.Sc.; F. R. Lankshear, B.A.

Professor of Metallurgy.—H. C. Carpenter, M.A., Ph.D.
Lecturer in Electro-Chemistry.—J. N. Pring, D.Sc.

The Session begins October 4, 1911.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Students commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Directors of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry.—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry.—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and R. Robison, Ph.D., B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 2nd, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a

course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, D.Sc., M.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.; J. Kenner, Ph.D., B.Sc.

The Session will commence October 4th.

Matriculation Course.—Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B.—Monday, Wednesday, Thursday, and Saturday at

9.30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B.Sc. Course in Chemistry.—Monday at 9.30 a.m. and Tuesday at 12.30 p.m. during second year, £3 3s.; Wednesday at 12.30 a.m., during two terms, Thursday at 10.30 a.m. and Friday at 10.30 a.m., during third year, £4 4s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five years' standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one-half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry (including Practical Physics) which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

DEPARTMENT OF METALLURGY.

Professor—J. O. Arnold, D.Met.

Assistant Professor—A. McWilliam, M.Met.A.R.S.M.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of

the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Department is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots. Differential annealing furnaces and gas and electric hardening furnaces constitute part of the plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—Hugh Marshall, D.Sc., F.R.S.
Assistant Lecturers—J. K. Wood, D.Sc. and (Vacant).
Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.
The Session consists of three Terms:—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The Junior Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First Professional).

The Intermediate and Advanced Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Technological Work or Research.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.
Lecturer on Physical Chemistry—Francis W. Gray, M.A., D.Sc.
Demonstrator—Joseph Knox, D.Sc.

I. General Lecture Course (100 Lectures).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. Physical Chemistry (60 Lectures).—Three Lectures a week on Physical Chemistry are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

III. Inorganic Chemistry (40 Lectures).—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

IV. Special Lecture Course on Organic Chemistry (50 Lectures).—Daily during the Summer Session. Fee, £3 3s.

V. Practical Course for Medical Students.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

VI. Chemical Laboratory.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; A. J. Findlay, M.A., B.Sc. (Agr.), N.D.A., N.D.D.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. Agricultural Chemistry (General Course).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. Laboratory.—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m.

for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—James Walker, LL.D., D.Sc., Ph.D., F.R.S.
Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; W. W. Taylor, M.A., D.Sc.; and J. E. Mackenzie, Ph.D., D.Sc.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, May to July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—Complex Qualitative Analysis; Preparations; Gravi-

metric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—A. Archibald Boon, B.A., D.Sc.; Andrew King, F.I.C.; Wm. Maitland, D.Sc.; F. D. Miles, B.Sc.

The Session begins Oct. 10th, 1911.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Analytical and Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University of Edinburgh as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.

Lecturer on Dyeing—A. B. Steven, B.Sc.

Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C.S.

Professor of Metallurgy—A. Campion, F.I.C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 26.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College (established 1796), the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses

extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1911-1912 may be had from the Director, Mr. H. F. Stockdale; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD.

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc. The Session begins on October 10th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-seven Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 4th and following days. Twenty-two of these Bursaries are restricted to Men, one is open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academic year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam. for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the pro-

ficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £5 5s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity of conducting original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851, Exhibition and Carnegie Research Scholarships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. W. Stewart, D.Sc.

I.—*Chemistry*.—The lectures are delivered at 12 o'clock, on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £3 3s.

II.—*Practical Chemistry*.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3 3s.

III.—*Laboratory Pupils*.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the beginning of July, on the first five days of the week, from 10 a.m. until 6 p.m. Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for three terms.

Scholarships.—The following College Scholarships are awarded specially in connexion with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

UNIVERSITY COLLEGE, CORK.

A CONSTITUENT COLLEGE OF THE NATIONAL UNIVERSITY OF IRELAND.

Professor—Augustus Edward Dixon, M.D.

Demonstrators—John Taylor, M.Sc.; James L. McKee, B.A., Ph.D.

The College Session will commence on October 20th, 1911, and end on June 30th, 1912. All classes are open to male and female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.

2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.

3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.

4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.

5. Courses in Systematic and in Practical Chemistry for Students of Engineering.

6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations ex-

tracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND. UNIVERSITY COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrator—A. G. G. Leonard, B.Sc., Ph.D., and Miss R. Clarke, B.A.

Research Assistant—Frederick G. Shephard, B.Sc., A.R.C.Sc.

The Session commences in October and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple gravimetric quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical fatty and aromatic organic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses.*—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo-chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—*First Year's Course.*—Same as Faculty of Science.

Faculty of Medicine.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates, and the chemical examination of urine. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—*First Year's Courses.*—Laboratory: Same as in Faculty of Engineering, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, first year.

The College offers a Scholarship in Chemistry for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and

Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitions, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for three years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION (F.I.C. AND A.I.C.).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to elevate the profession of Chemistry by setting up a high standard of scientific and practical proficiency for persons desirous of becoming professional consulting and technological chemists, public analysts, and chemical advisers; by examining Candidates, and granting certificates of competency; and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. A Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *The Final Examination* (Fee, £5 5s.) *for the Associateship (A.I.C.).*—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry; metallurgical

chemistry; physical chemistry; organic chemistry; chemistry of food and drugs, fertilisers and feeding-stuffs, soils, and water (including a compulsory examination in therapeutics, pharmacology, and microscopy); or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *Fellowship (F.I.C.)*. For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Bloomsbury Square, London, W.C. Past Examination Papers, 6d.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—I. S. Scott, F.I.C., F.C.S., and Assistants. Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School. Session commences October 2nd.

BATTERSEA POLYTECHNIC.—Principal, Mr. S. G. Rawson, D.Sc., F.I.C. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), F.I.C., and Assistants. Session opens Sept. 25. Complete courses of instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Technical Bacteriology, Paper Making and Testing, and Oils, Fats, and Soap, Chemical Engineering, Dyeing and Cleaning, Food and Drugs Analysis, and Pharmacy and Dispensing.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. Duffie, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro-chemistry and Electro-chemical Analysis. Special Course of Lectures on Chemistry and Technology of the Essential Oils, by C. T. Bennett, B.Sc., A.I.C. Special Lectures and Laboratory Courses on the Chemistry and Manufacture of Food-stuffs, by Edward Hinks, B.Sc., F.I.C., and Thomas Macara, F.I.C., F.C.S. Special Course on Analysis of Laundry Trade Materials. Session opens Monday, Sept. 25.

BIRKBECK COLLEGE, Breems Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Wednesday, Sept. 27, when Sir William Tilden, D.Sc., F.R.S., will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. Last session 47 students took Degrees in Arts and Science, 21 with Honours. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Principal, R. S. Clay, D.Sc.; Head of the Chemical Department, W. H. Mills, M.A., Sc.D.; Assistants, W. H. Watson, B.Sc., A.R.C.S.; Miss A. M. Bain, M.A., B.Sc.; and F. W. Lynch, B.Sc., A.I.C. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. The Session begins Sept. 18. Prospectus sent free on application to the Secretary.

NORTHAMPTON POLYTECHNIC INSTITUTE, St. John Street, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c.; Technical Chemistry, Mr. S. Field, A.R.C.S.; Mr. A. H. Munday, F.C.S.; Mr. E. B. Ware; and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus).

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and

B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of four years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, *id.*, by post 4d.

EAST LONDON COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S. Lectures and Practical Classes are held, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to Research and Post-graduate studies. Evening Classes for London University Degrees are also held.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Biology, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I.C., Arthur R. Ling, F.I.C., A. R. Smith, M.Sc., F.C.S., C. O. Bannister, A.R.S.M., Arthur Harden, D.Sc., J. S. S. Brame, and Wesley J. Lambert. The Session of the Sir John Cass Technical Institute will commence on Monday, September 25th. The Institute, which was founded by the Governors of Sir John Cass's Foundation, is specially devoted to technical training in experimental Science and in the Artistic Crafts. Graded curricula of study, extending over several years, are provided in the several departments of work, and in addition a number of special courses of instruction given by experts, so that there are full educational facilities in the subjects taught, both for youths and for those who have had no previous systematic training, and also for those holding responsible positions who desire to keep in touch with modern developments of the applications of science to industry. Amongst the special features of the syllabus for the new Session are courses of instruction on "Liquid, Gaseous, and Solid Fuel," arranged to meet the requirements of those engaged in chemical and engineering works or who are concerned with the use of fuel as a motive power; on the Fermentation Industries, including a special course on the Microbiology of the subject; on the various branches of Metallurgy, and on Scientific and Technical German. The aim of this last course is to provide for those engaged both in Pure and in Applied Science with an opportunity of acquiring a knowledge of scientific and technical terms employed in German with the view of enabling them to read German scientific and technical works and literature. Full details may be obtained on application, or by letter to the Principal.

EAST HAM TECHNICAL COLLEGE.—Principal, W. H. Barker, B.Sc. Chemistry, A. E. Dunstan, B.Sc. Evening Classes and Secondary School.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc. (Lond.), &c., assisted by Messrs. Jos. Yates, M.Sc., F.I.C., W. O. Littlebury, B.Sc., F.I.C., Jos. Kenyon, B.Sc., A.I.C., and W. A. Jowitt. Session opens Monday, Sept. 18. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

LEEDS: CENTRAL TECHNICAL SCHOOL, Leeds Institute, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in all

subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, Mr. A. McFarlane, and Mr. O. F. Kirby, M.A., B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Gas Manufacture, by Mr. W. E. Pettigrew; Oils and Fats, by Mr. W. Dillon; Magnetism and Electricity, Practical Physics, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Bread-making and Flour Confectionery, by Messrs. W. H. Quinn and J. C. Hesselgrave; Photography and Process Work, by Mr. S. E. Bottomley and Mr. A. Guy Symmons. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Special three evening Course for Pharmaceutical Students, covering the "Minor" syllabus in three years, by Messrs. J. H. Gough, Ph.C., F.C.S.; S. Parrish, B.Sc., A.R.C.S.; and N. Walker. Session commences Sept. 18th. See the Technical Handbook, 2d. (by post 5d.). Prospectuses of various Classes free on application to the Head Master, or to Mr. James Graham, Secretary for Education, Calverley Street, Leeds.

REDRUTH SCHOOL OF MINES (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile industries, Photography, Collotype and Photo-mechanical processes, Letterpress and Lithographic industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity. The School is established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science B.Sc. and M.Sc. Tech.). Special facilities are offered to graduate students desirous of pursuing advanced research in any department of Applied Chemistry and other branches of the Industrial Arts, and a Journal is published embodying the more important results of such researches. The Session commences Sept. 18.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Principal, J. W. Coales, D.Sc., M.I.E.E.; Inorganic and Organic Chemistry, Mr. Th. J. Murray, M.Sc., Ph.D.; Physics, Mr. A. T. Harrison, B.Sc.; Botany, Mr. Sidney Phillips, Ph.C. Human Physiology and Hygiene, Mr. H. J. Tench, A.R.S.I. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. Session commenced Monday, Sept. 12th. For other particulars and programme, apply Mr. G. F. Chell, Secretary.

MUNICIPAL TECHNICAL INSTITUTE, BELFAST.—Principal, F. C. Forth, A.R.C.Sc.I. Chemistry, Prof. H. Wren, M.A., Ph.D., D.Sc., and Assistants. Day and Evening Courses. Session opens Sept. 11th.

NOTICES OF BOOKS.

Triumphs and Wonders of Modern Chemistry. By GEOFFREY MARTIN, B.Sc. (Lond.), M.Sc. (Bristol), Ph.D. (Rostock). London: Sampson Low, Marston, and Co., Ltd. 1911. (7s. 6d.).

THE author of this book shows unusual skill in putting his matter before his readers in such a way as to appeal most to the imagination, and it would be a very dull young student who read it without becoming something of an enthusiast in his scientific work. Many a teacher also will gain fresh ideas from it which will add to the vividness and interest of his lessons, the author's speculations and illustrations having invariably the charm of great originality. The earlier chapters deal with modern theories of matter, the atom and molecule and their structure, and the evolution of the elements. Later chapters discuss the individual elements and some important compounds, such as water and carbon dioxide, and as a good example of the author's attractive style may be mentioned the description of the life history of a phosphorus atom, from its birth "out of the vast into the great sea of ether," and its youth in the heart of a rock, to its passage into the structures of plants and animals. The book bears to the ordinary text-book of chemistry the same relation as a historical novel to a school history book, with the difference that the text is not merely founded on fact, but describes the well authenticated results of the researches of the most eminent scientific men. It is regrettable that some of the illustrations are not more worthy of the text.

Report of the Indian Association for the Cultivation of Science for the Year 1909. Calcutta: P. Sircar. 1911.

THIS Report of the Indian Association for the Cultivation of Science contains an account of the Thirty-third Annual Meeting of the Association, held in December, 1910, together with some notes on the analytical work which has been done in the laboratory. This work consists chiefly of routine analyses of articles of food, drugs, water, &c. Some meteorological observations and charts are also reproduced in the Report.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 26, June 26, 1911.

Action of Silent Discharge on Dry and on Wet Ammonia.—A. Besson.—When a silent discharge acts on dry ammonia the latter is partially decomposed into nitrogen and hydrogen. If the gas is diluted with pure dry hydrogen a very small amount of hydrazine is formed. In the presence of moisture the reaction is $\text{NH}_3 + \text{H}_2\text{O} = 2\text{H} + \text{NH}_2\text{OH}$.

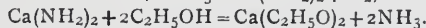
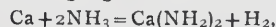
Catalytic Etherification of Aromatic Acids.—J. B. Senderens and J. Aboulenc.—The aromatic acids can be divided into two classes according to the effect of sulphuric acid, potassium bisulphate, and aluminium sulphate on their etherification. (1) For those in which the carboxyl is directly attached to the benzene radicle the formation of hydrates is the chief factor which favours etherification. (2) For those in which the carboxyl is separated from the benzene radicle by fatty chains (e.g., phenyl acetic acid) temporary compounds are formed with the alcohols by the catalysers.

Bulletin de la Société Chimique de France.

Vol. ix.-x., No. 12, 1911.

The Dissolved Molecule and van't Hoff's Hypothesis.—Albert Colson.—The author finds that the lowering of the freezing-point produced by $\text{H}_2\text{SO}_4 \cdot [\text{ZnSO}_4]_2$, $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_4\text{O}(\text{SO}_4)_5$, respectively, dissolved in 10 litres of water, is practically constant, and does not depend upon the degree of ionisation of the dissolved salts. The dissolved particle is generally an aggregate of chemical molecules in accordance with Raoult's laws, but independent of the degree of ionisation if it is measured by the classical conductivity method. This result agrees with Cahour's fundamental principle.

Hydrogenation by Calcium and Absolute Alcohol.—Pierre Breteau.—Phenanthrene is not hydrogenated by calcium and absolute alcohol, but excellent results are obtained if an alcoholic solution of ammonia is used. Calcium amide is first formed, and is then converted into ethylate, ammonia being regenerated:—



Phenanthrene can thus be totally transformed into the tetrahydride.

Action of Hydriodic Acid on Starch and Dextrine.—Echsnier de Coninck and M. Raynaud.—Hydriodic acid is capable of saccharifying starch and dextrine, and the degree of saccharification is practically directly proportional to the amount of acid used. As with other acids it is possible to reach total saccharification. The action occurs more easily with dextrine than with starch, the weight of glucose formed with the same amount of acid being always higher with dextrine than with starch.

Ketodiacyds.—E. E. Blaise and H. Gault.—When 2 molecules of oxalic ether condense with 1 molecule of dioxalsuccinic ether and the product is saponified, two heterocyclic products are formed in succession, oxyprone carbonic acid and isopyromucic acid. Dioxalsuccinic acid appears to be a δ - and not a γ -lactone.

Bromination of Cyclohexane.—F. Bodroux and F. Taboury.—Under the ordinary pressure, and at the boiling-point of cyclohexane (81°), the latter is slowly attacked by bromine in diffused light, an insignificant quantity of hydrobromic acid being set free. Under the influence of direct sunlight bromine acts energetically on cyclohexane, cyclohexyl bromide being formed and some polybrominated compounds. The ultra-violet rays do not favour the bromination of cyclohexane. By employing a higher temperature it is possible to obtain dibromocyclohexane.

Bromination of Hydroaromatic Compounds in presence of Aluminium Bromide.—F. Bodroux and F. Taboury.—By the bromination of cyclohexane in presence of aluminium bromide, the authors did not obtain the solid product described by Kijner and Markownikof, but a viscous liquid from which no definite compound could be isolated. Cyclohexane readily yields hexabromobenzene, and methylcyclohexane is partially transformed into pentabromotoluene. Dimethylcyclohexane yields a mixture of several tetrabromoxylenes.

Oxyindazols.—P. Freundler.—The action of PCl_5 on benzene-azo-o-benzoic acid gives a mixture of the chlorinated derivatives with the chlorine in the 5- and 3-positions respectively. When this mixture is oxidised the product is a mixture of the two isomeric chlorinated azoic acids, from which the 3,5-dichloro-oxy-indazol is obtained by the action of PCl_5 .

Chlorinated and Brominated Anthranilic Ethers.—P. Freundler.—Methyl anthranilate can be chlorinated by dissolving it in a mixture of acetic acid and hydrochloric acid, and passing in a current of pure dry chlorine for about four hours. The dichlor-derivative is thus precipitated, and the monochlor-derivative remains in solution in the mother-liquor. The same method cannot be used

for bromination, but good yields are obtained by allowing bromine to act on the compound of chloral with the amino-derivative. The author gives a brief description of the properties of the two chloro- and bromo-derivatives of methyl anthranilate.

Alcoholysis of Japan Wax.—E. Tassily.—Under the name "alcoholysis" a new method of studying fatty substances has been described by Haller. It consists in heating the fatty body with alcohol and anhydrous ether. When it is applied to japan wax it is found that the chief constituents are palmitine and free palmitic acid. The wax also contains jpanic acid, $C_{14}H_{38}(CO_2H)_2$, and its two lower homologues, as well as small quantities of soluble acids, isobutyric acid being very probably among them. Pelargonic acid, an acid $C_{15}H_{30}O_2$, and traces of stearic and oleic acid are present, but not arachidic acid.

Complete Destruction of Organic Matter.—Pierre Breteau.—Before proceeding to examine foods, &c., for mineral poisons it is necessary to destroy the organic matter present in them. This may be done by adding 300 cc. of pure sulphuric acid and 0.2 gm. of copper sulphate to 300 grms. of the substance and passing nitrous vapours through the gently heated liquid. The nitrous vapours may be produced by passing a current of sulphur dioxide, obtained from the liquid anhydride, through nitric acid. The action is continued until a colourless or pale straw-coloured liquid is obtained.

Determination of Tannin in Wine.—Philippe Malvezin.—Ten cc. of the wine are boiled with 10 cc. of an ammoniacal solution of zinc acetate made by dissolving 10 grms. of precipitated zinc oxide in acetic acid, adding 80 cc. of ammonia, and making up to a litre with water. The precipitate obtained is dissolved by washing with sulphuric acid, containing 2.5 cc. of pure H_2SO_4 in 100 cc. of water, and the acid is then titrated with 10 per cent chameleon solution. If n is the number of cc. used $n \times 0.116$ = tannin in grms. of gallo-tannin per litre.

MISCELLANEOUS.

Chemical Laboratory Fresenius, Wiesbaden, Germany.—At the vacations course held in the Spring, 1911, at the Chemical Laboratory Fresenius, twenty-three students took part. During the regular Summer term, 1911, the laboratory was attended by thirty-six students, including five ladies. The nationality of the students was as follows:—Twenty-four Germans, four Russians, two Frenchmen, two Spaniards, one Englishman, one Hollander, one Dane, and one Norwegian. Besides the Directors, Geh. Regierungsrat Ptof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, and Prof. Dr. E. Hintz, there are four duly qualified lecturers and heads of departments; there are also two assistants in the Instruction Laboratory, and twenty-eight assistants and sub-assistants in the Private Laboratories (Versuchsstationen). The next Winter Term will begin on October 16th. During the Summer, 1911, an Electro-analytical Department was added to the Laboratory Fresenius. This is on the same lines as the Electro-analytical Laboratory at Aachen, excellently fitted out; it answers all up-to-date requirements, and offers opportunity for the execution of electro-analytical work of every description, especially for rapid methods. The head of this section is Dr. R. Fresenius. During the Summer, 1911, a number of scientific treatises originated from the Laboratory Fresenius; they were published in different chemical journals. As special print appeared:—"Chemische Untersuchung der neuen Quelle zu Brambach im Vogtlande, sowie Untersuchung derselben auf Radio-aktivität, von Geh. Regierungsrat Prof. Dr. H. Fresenius, Wiesbaden, C. W. Kreidel's Verlag, 1911." Besides the scientific work a great number of chemical analyses were executed during the Summer half-year 1911 for commercial, mining, industrial, and agricultural purposes, also in the interest of Sanitary-boards, Criminal, and other States Departments.

MACMILLAN'S NEW and RECENT BOOKS ON CHEMISTRY.

FOURTH EDITION, Completely Revised.

A TREATISE ON CHEMISTRY.

BY
Sir H. E. ROSCOE, and C. SCHORLEMMER,
F.R.S. F.R.S.

VOL. I.—The NON-METALLIC ELEMENTS. New Edition. Completely Revised by Sir H. E. ROSCOE, assisted by Dr. J. C. CAIN. Illustrated. 8vo. 21s. net.

CLASS BOOK OF CHEMISTRY.

By G. C. DONINGTON, M.A.

Part I., 1s. 6d. Parts II. and III., 2s. 6d.
Complete, 3s. 6d.

All the subjects included in the new syllabus in Chemistry for the Matriculation Examination of the University of London are dealt with in this book.

SCHOOL WORLD.—"The volume is most appropriate for classes in secondary schools and for junior classes in technical schools, and it possesses the advantage of meeting the requirements of both class-room and laboratory. The experiments are quite simple, and frequently exhibit novelty of method combined with improved efficiency. The illustrations are excellent."

TECHNICAL JOURNAL.—"The book is one that can be strongly recommended for use as a class-book in schools."

LABORATORY NOTES ON ORGANIC CHEMISTRY FOR MEDICAL STUDENTS.

By PAUL HAAS, D.Sc., Ph.D.

Crown 8vo. 2s. 6d. net.

ST. GEORGE'S HOSPITAL GAZETTE.—"A distinctly useful book. . . . In a university or a hospital which possesses a good chemical laboratory, this book would be invaluable."

THIRD EDITION. NOW READY.

ESSAYS IN HISTORICAL CHEMISTRY

By Sir EDWARD THORPE,

C.B., LL.D., F.R.S., &c.

8vo. 12s. net.

Contains Lives of R. Boyle, J. Priestley, C. W. Scheele, H. Cavendish, J. Watt, A. L. Lavoisier, M. Faraday, T. Graham, F. Wöhler, J. B. A. Dumas, H. Kopp, V. Meyer, D. I. Mendeleeff, S. Cannizzaro, and J. Thomsen.

THIRD ENGLISH EDITION.

Theoretical Chemistry
from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. WALTER NERNST, Ph.D. Revised in accordance with the Sixth German Edition by H. T. TIZARD. Third English Edition. 8vo. 15s. net.

Applied Electrochemistry.

By M. de KAY THOMPSON, Ph.D., Assistant Professor of Electrochemistry in the Massachusetts Institute of Technology. Illustrated. 8vo. 9s. net.

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. CIV., No. 2704.

THE RATE OF COAGULATION OF COLLOIDAL COPPER.*

By H. H. PAINE, M.A., B.Sc.

THE copper colloidal solution studied was prepared by Bredig's electrical method, a positive hydrosol being thus obtained. The coagulation of this solution by means of simple salts, such as sodium sulphate or potassium nitrate, appears to be a gradual process. The precipitated gel can be separated from the solution by allowing it to settle; the clear liquid containing the copper not yet coagulated can then be drawn off. The amount of copper present can be determined volumetrically by titrating in the warm with dilute nitric acid, the disappearance of the colour of the liquid indicating the complete solution of the copper by the equivalent quantity of acid. This estimation of the copper still in colloidal solution can be made after definite intervals of time from the addition of the salt. The course of the coagulative process can thus be studied.

The following results among others were obtained:—
(1) There is an initial period during which the solution remains clear and no coagulation takes place. (2) Using colloidal solutions of various concentrations, the rate of precipitation is proportional to the square of the initial concentration for the irreversible coagulation produced by salts containing a divalent anion (sodium sulphate). For salts containing monovalent anions (potassium nitrate or sodium chloride) the coagulation is not irreversible, and a more complicated relation holds. (3) For varying amounts of the electrolyte, the rate of coagulation is proportional to some power of the concentration of the salt; *i.e.*, if we increase the concentration of the salt proportionally, the rate of the coagulation will be increased proportionally also.

THE ADSORPTION OF IODINE BY THE GLUCOSIDE SAPONARIN.*

By Dr. GEORGE BARGER.

SAPONARIN is a glucoside occurring in *Saponaria officinalis* and other plants; it has the composition $C_{21}H_{24}O_{12}$ (Mwt = 468), and is obtained pure by crystallisation from pyridine. It has been fully characterised chemically (*Journ. Chem. Soc.*, 1906, lxxxix., 1210), and has been shown to yield on hydrolysis glucose and the colouring matter vitexin (first isolated by A. G. Perkin, *Journ. Chem. Soc.*, 1898, lxxiii., 1030). Saponarin was first known to botanists as "soluble starch," on account of the blue coloration given by its solutions on addition of iodine dissolved in potassium iodide. When the pure crystalline substance is shaken with water at room temperature, a solution is formed containing about 1 part in 7000, which is not coloured blue by iodine. The solubility in boiling water is about 1 : 1000; on cooling, the glucoside does not crystalline out for some days, but remains dissolved as a colloidal solution, and this solution closely resembles a solution of soluble starch as regards its behaviour towards iodine. A more concentrated hydrosol can be produced by acidifying a solution of the glucoside in alkali, in which it is readily soluble; but this, of course, introduces a salt. In the cell-sap of *Saponaria* the substance is held in solution by Saponin. In order to obtain a pure hydrosol, free from other substances, it is best to boil the glucoside with water in a quartz vessel.

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911

The aqueous solutions of saponarin, obtained by any of the above methods, are seen to be colloidal when examined ultra-microscopically. The alkaline solutions appear to contain particles of various sizes; neutralisation is marked by the appearance of a large number of small particles. The author is indebted to Dr. W. M. Bayliss, F.R.S., for these observations.

As in the case of starch, the addition of a pure aqueous iodine solution to the hydrosol does not bring about a blue coloration, which, however, appears on the addition of potassium iodide. It is found that in the present case many other salts (ammonium chloride, aluminium sulphate) are also effective. The blue colour disappears on the addition of organic solvents or of sodium thiosulphate; also (temporarily) on heating.

If, together with the iodine, but little salt is added, the blue adsorption compound remains dissolved, but the further addition of electrolytes causes flocculation and the separation of a dark blue gel. The concentration of salt required depends primarily on the cation, and is in accordance with Schulze's law. Thus in a given case for a number of K, Na, NH_4 salts this concentration was 0.053 grm. equivalents per litre, for Ba, Ca, Sr about 0.0047, and for Al salts 0.006. If electrolytes are excluded as far as possible, the blue hydrosol does not travel appreciably with a current of 110 volts.

The conductivity of the blue hydrosol is less than that of the potassium iodide contained in it. So that some of the salt is probably adsorbed, and this salt, or its cation, favours the adsorption of iodine by saponarin, just as cations facilitate the absorption of congo red by filter-paper (Bayliss, *Biochem. Journ.*, 1906, i., 175). Owing to experimental difficulties it has not yet been possible to determine the effect of the valency of the cation.

The iodine content of the blue hydrogel depends on the concentration of the iodine left in aqueous solution, as was shown for starch by Küster (*Annalen*, 1894, cclxxxiii., 360), and for basic lanthanum acetate by W. Biltz (*Ber.*, 1904, xxxvii., 719).

Preliminary experiments yielded the following results:—

C_w .	C_s (found).	C_s (calc.).
0.0000533	0.080	0.073
0.000171	0.109	0.110
0.000376	0.124	0.126
0.000606	0.131	0.132
0.000792	0.133	0.133

Here C_w represents the free iodine (in grms.) remaining in 1 cc. of water and C_s the iodine precipitated with 1 grain of saponarin. The third column is calculated according to the formula $C_s = A C_w^a$; where $a = 0.47$ and $n = 0.166$. The value for n is much smaller than is generally the case with solid adsorbents (*e.g.*, charcoal). It is apparently somewhat higher in very dilute solution. The formula does not apply to concentrated solutions of iodine, for which n falls off much below 0.166.

THE THEORY OF COLLOIDS.*

By Prof. H. FREUNDLICH.

THE classical researches of Graham pointed to a fundamental difference between crystalline and colloidal substances. The work of Zsigmondy with the ultramicroscope proved colloidal solutions to be two-phase systems, containing suspended particles. The quantitative experiments of Perrin and of Svedberg, dealing with the Brownian movement, proved the colloidal solutions to form a connecting link, without any sharp discontinuity, between coarse suspensions on the one hand and true solutions on the other, although the differences between the extreme terms

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

of the series are very marked. Recent work on true solutions, especially in respect to colour and solubility, indicates that the simple theory of van't Hoff fails to take account of certain important factors, notably of the combination of the dissolved substance with the solvent which undoubtedly occurs in true solutions. On the other hand, coarse suspensions are only formed by very sparingly soluble substances, which have little tendency to react with the solvent. Colloidal solutions stand between these two extremes. One class, distinguished from coarse suspensions only by the ultramicroscopic dimensions of their particles, are termed "Suspension-colloids" or "Lyophobic Sols." These include colloidal metals, sulphides, and many hydroxides. "Emulsion-colloids," or "Lyophilic sols," which include albumin, gelatin, starch, &c., approach more nearly to the true solutions. The members of this latter class are far more irregular in their behaviour than those of the former.

The question, whether the particles of colloidal solutions are necessarily amorphous, is not easily answered, and it is not yet known how far a crystalline solid may be subdivided and yet retain its crystalline properties. The particles of many colloidal solutions approach molecular dimensions, and it cannot be assumed without proof that they retain the properties of the corresponding phases in larger mass. In many cases the particles are certainly amorphous.

Adsorption is chiefly manifested by amorphous substances, and the substances adsorbed are frequently of high molecular weight. It remains uncertain whether adsorption is an effect of surface condensation, solid solution, or chemical combination, although the author inclines towards the first of these views. Owing to the great adsorbing power of amorphous substances, it is almost impossible to obtain a pure colloidal solution. The tendency of small particles to become larger, and to be transformed into crystals, is greatly lessened by the presence of absorbed impurities. Thus the amorphous condition of the particles favours adsorption, and this again favours the maintenance of the colloidal state. Other factors affecting the stability are the internal friction of the liquid and the electrical charge on the particles.

The electrical charge is of importance in the coagulation of suspension colloids, the addition of an electrolyte, by discharging the particles, facilitating coagulation. When the sol is positively charged, as in colloidal metallic hydroxides, the order of influence of coagulating agents is the reverse of that which is found with negatively charged sols, such as colloidal metals and sulphides. A series of experiments by Elisaff and the author on the influence of electrolytes in diminishing the electroendosmosis of a solvent shows that a complete parallelism exists between this effect and the discharging effect of the same electrolytes on a hydrosol.

In the case of emulsion colloids, electrical conditions are of far less importance, and the determining factors are chiefly the individual characters of the substances concerned.

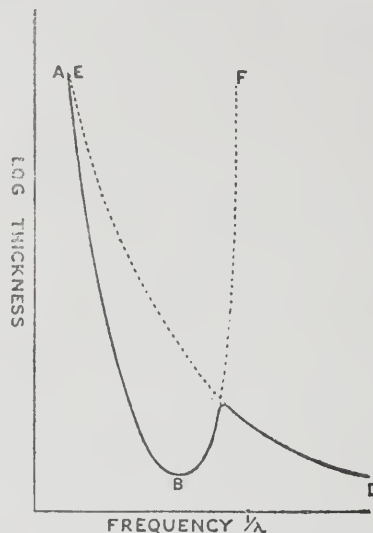
In conclusion, attention is drawn to the importance of colloidal chemistry, or, in a wider sense, of capillary chemistry, in its bearings on physiological problems.

DYNAMIC ISOMERISM.*

General and Specific Absorption.

NEARLY all carbon compounds absorb light to a considerable extent in the far ultra-violet. If the thickness of the column of liquid be diminished the limit of transmission extends, as a rule, progressively in the direction of the

visible region; on plotting the thickness against the limit of transmission ($1/\lambda$) a curve DCE of general absorption is obtained in shape resembling, roughly, a portion of a parabola. In addition to this general absorptive power, many liquids have the property of absorbing specifically light of a particular wave-length; but this absorption (unlike the line-spectra of vapours) covers a considerable range of wave-lengths on either side of the maximum absorption; this range increases as the thickness of the liquid is increased, so that the curve ABF of "specific" absorption is somewhat of the shape of a narrow parabola. As the curve of general absorption intersects the curve of



specific absorption at different distances on the axis "thickness," the arms of the parabola are unequal in length, the complete curve being generally of the form ABCD. The point B is the "head" of the band; the thickness at which it occurs under given experimental conditions is a measure of the "penetration" of the band, whilst the range of thickness from B to C is a measure of its "persistence." Both quantities are conveniently measured in terms of "log. thickness in millimetres of millinormal solution," e.g., if B = 10 mm. and C = 100 mm. then—

$$\log. \text{ penetration} = 1.0$$

$$\log. \text{ persistence} = 2.0 - 1.0 = 1.0.$$

It will be noticed that the depth of penetration of the band is the best measure of the intensity of the local absorption, whilst the persistence, which depends on the relationship of the local to the general absorption, is likely to be greater when the head of the band occurs at a low than at a high frequency.

In classifying absorption-spectra it has been customary to draw a sharp distinction between those substances which produce only a "general" absorption of light and those which give rise to definite absorption "bands." It has even been suggested that this property might be used to classify carbon compounds into two groups, one group characterised by a "fixed" structure, and giving rise to general absorption, the other group including "labile" compounds undergoing isomeric change readily, and giving rise to banded spectra. The impracticability of this demarcation was shown in the report presented at Winnipeg in 1909, in which an account was given of several labile compounds which gave "continuous" absorption curves, whilst certain compounds of fixed structure were shown to produce "banded" absorption.

In the report presented at Sheffield in 1910 the origin of banded spectra was considered, special attention being directed to those alterations of molecular structure which

* Report of the Committee, consisting of Prof. H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Prof. Sydney Young, Dr. C. H. Desch, Dr. J. J. Dobbie, Dr. M. O. Forster, and Dr. A. Lapworth. (Drawn up by the Secretary). Read before the British Association (Section B), Portsmouth Meeting, 1911.

have the effect of increasing or diminishing the intensity of the local absorption. It was found that by reducing the residual affinity of the absorbing centres an absorption band could be driven back almost to the extreme limit of oscillation-frequency at which it can be photographed by ordinary methods, and that any further weakening of the absorbing centres had the effect of converting the banded into a general absorption. The view was therefore adopted that a curve of general absorption might be produced by a band situated in such a position as to be inaccessible to ordinary methods of observation, say, at $1/\lambda$ 4200 or beyond.

During the past year attention has been directed to the study of general absorption, and attempts have been made to determine the approximate positions of the inaccessible bands to which this type of absorption curve appears to be due. The method adopted depends on the well known fact that most of the optical constants of a substance increase with great rapidity when an absorption-band is approached, and appear to tend towards an infinite value in the case of a sharply-defined absorption-line. In applying this method to carbon compounds the magnetic rotatory dispersion has been found to be a very convenient property to discuss, and measurements of this kind have been used to calculate the limit of transmission for a large number of substances; in other words, the position of the heads of the inaccessible bands by which the general absorption is produced. Typical values are as follows:—

	λ .	$1/\lambda$.
Methyl and ethyl alcohols	1300	7500
Propyl alcohol, normal esters	1350	7400
Fatty acids, higher ketones, glycol, glycerol	1380	7200
Higher alcohols (<i>fr.</i> and <i>sec.</i>)	1400	7100
Water, acetone, <i>ter.</i> alcohols	1500	6700
Allyl alcohol	1700	5800
Phenyl ethyl carbinol	2000	4900
Carbon disulphide	2200	4350

The chief points to be noted are:—

1. That the optical properties of the majority of saturated carbon-compounds are determined mainly by an absorption in the far ultra-violet at wave-length 1300 to 1400; this appears to represent the extreme limit of transmission in the case of all compounds containing carbon, hydrogen, and oxygen.

2. The shallow absorption-bands which appear in the near ultra-violet region at wave-lengths from 3000 to 4200 in the case of substances such as acetone, are almost without influence on the optical properties of these substances in the visible region.

3. The dominant absorption may, however, be brought nearer to the visible region by introducing an ethenoid linkage, as in allyl alcohol, or a benzenoid nucleus as in phenyl ethyl carbinol; but in none of the simple compounds of which the magnetic rotatory dispersion has been determined does the dominant absorption fall within the region usually photographed in the study of absorption spectra.

ELECTRO-ANALYSIS.*

ATTENTION has been directed during the past year particularly to the application of the electrometric method to the titration of weak acids in such liquids as tan liquors. It was found that the potentiometer box and auxiliary electrode constructed for the separation of metals by graded potential may be conveniently employed for this purpose in conjunction with a form of hydrogen electrode specially designed to combine ease of manipulation and rapidity of saturation. The question regarding the "end-point" of the titration has been examined. It is known

* Report of the Committee, consisting of Professor F. S. Kipping (Chairman), Dr. F. M. Perkin (Secretary), Dr. G. T. Beilby, Dr. T. M. Lowry, Professor W. J. Pope, and Dr. H. J. S. Sand. (Drawn up by Dr. H. J. S. Sand). Read before the British Association (Section B), Portsmouth Meeting, 1911.

that if the object of the titration be to determine the number of equivalents of acid present, then not only the nature of the acid or acids must be considered, but also the concentration of the salts resulting from the titration. It has been pointed out, however, that in most practical cases it will be possible to fix end-points of special importance for the particular purpose in question. Frequently the liquid may be titrated until the hydron-concentration of pure water is reached. This corresponds to a potential difference between the hydrogen-electrode and the normal calomel electrode recommended for these titrations, of 0.69 volt. (See Part I. *Journ. Soc. Chem. Ind.*, in conjunction with D. J. Law, 1911, xxx., 3; reprinted in full *Journ. Amer. Leatherchemists Assn.*, 1911, cxiv.; and *Ledermarkts Kollegium*, 1911, p. 150, Part II., in conjunction with J. T. Wood and D. J. Law; *Journ. Soc. Chem. Ind.*, July 31, 1911).

By Dr. F. Mollwo Perkin.—It has been found possible by Hildebrand (*Chem. Zentralblatt*, 1907, ii., 8) and E. F. Smith and his co-workers to electrolyse the alkali metals with a mercury cathode and to analyse both the anion and cation. For this purpose a double cell is employed, the inner and outer portion being sealed by means of mercury. The alkali salt to be analysed, say potassium sulphate, is placed in solution in the central cell where an anode of platinum gauze is rapidly rotated. The outer cell contains water with a small quantity of sodium chloride solution to make it conductive. On electrolysis, the SO_4 anions are discharged at the anode and a solution of sulphuric acid obtained. The K cations are discharged on the mercury which is made the cathode. Owing to the rotation of the anode the amalgam which is specifically lighter than the pure mercury is swept into the outer compartment, where it is decomposed by means of an auxiliary nickel cathode placed above the mercury in the solution. When the electrolysis is complete the SO_4 in the inner cell is titrated by means of standard alkali and the K in the outer cell by means of standard acid.

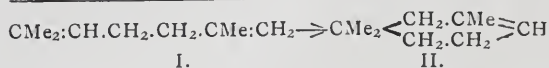
There are disadvantages in the apparatus of Hildebrand, the outer cell of which is a glass crystallising basin, the inner consisting of a beaker with the bottom cut off. The inner cell is kept in a central position by having corks wedged at the sides. F. M. Perkin has now had a vessel made of fused quartz. The centre cell is kept concentric by having quartz rods fused to it and to the inside wall of the outer basin. Being of quartz, the vessel can, for cleaning purposes, be heated to redness, is absolutely unattacked by alkali, and there are no corks which, if they get accidentally splashed, absorb some of the alkali and vitiate the results.

Experiments on the analysis of the anions and cations are being carried out with this apparatus, and the results so far have been encouraging.

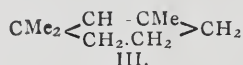
THE STUDY OF HYDRO-AROMATIC SUBSTANCES.*

Synthesis of Cyclogeraniolene (1:1:3-Trimethylcyclohexene) (Crossley and Gilling, *Journ. Chemical Soc.*, 1910, xcvi., 2218).—Some years ago Tiemann and Semmler (*Ber.*, 1893, xxvi., 2708) prepared from the aldehyde citral (geranial) an open-chain hydrocarbon, $\text{C}_{10}\text{H}_{16}$, named by them geraniolene. The constitution of this substance (I.) follows from that of citral, which was established by Barbier and Bouveault in 1896 (*Comptes Rendus*, cxvii., 393). When geraniolene is shaken with a 60 per cent solution of sulphuric acid, an isomeric change takes place, the open-chain hydrocarbon being converted into a mixture of two cyclic hydrocarbons α - and β -cyclogeraniolene (II. and III.), in which mixture the α variety is present in larger quantity,—

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Portsmouth Meeting, 1911.

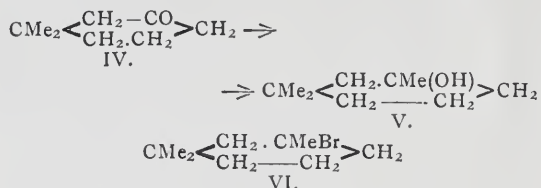


and—



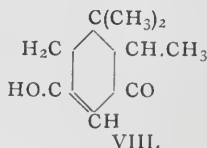
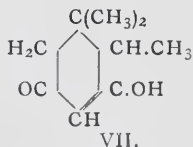
Constitutional formulæ were assigned to these hydrocarbons by Tiemann (*Ber.*, 1898, xxxi., pp. 816, 881; 1900, xxxiii., 3711), arrived at from a study of their oxidation with potassium permanganate, and these formulæ are proved to be correct by the following synthesis:—

1 : 1-Dimethylcyclohexanone (IV.) was treated with an ethereal solution of magnesium methyl iodide and the product decomposed with water, when trimethylcyclohexanol (V.) was obtained as a well-defined crystalline substance, melting at 72.5°—



Fuming hydrobromic acid converts the alcohol into 3-bromo-1 : 1 : 3-trimethylcyclohexane (VI.), which, when treated with alcoholic potassium hydroxide, loses the elements of hydrogen bromide in two ways, giving rise to the same mixture of hydrocarbons as described by Tiemann. The identity was established by preparing the crystalline nitrosate, and from it the oxime described by Wallach (*Ann.*, 1902, cccxxiv., 97); further, by oxidising the hydrocarbons with potassium permanganate, when the products isolated were *as*-dimethylsuccinic acid, *isogeronic* and *geronic* acids.

1 : 1 : 2-Trimethylcyclohexan-3-one (Crossley and Renouf, *Journ. Chem. Soc.*, 1911, xcix.).—Brief reference was made in the last Report (*Brit. Assoc. Report*, Sheffield, 1910, p. 82) to the method adopted for the preparation of this ketone, the object of its isolation being to compare its properties with those of camphor on account of the marked similarity of the various groupings in the molecules of these two ketones. Further, it was thought that a more extended inquiry into the chemical behaviour of trimethyldihydroresorcin than has hitherto been carried out was desirable because, unlike dimethyldihydroresorcin (VII.), its molecule is not symmetrical, and consequently several new points of interest are raised. This latter problem has proved to be more complicated than was anticipated, but there can be no doubt that trimethyldihydroresorcin is a tautomeric substance, exhibiting the two forms represented by formulæ VII. and VIII. :—



the particular form manifested depending on the nature of the reagents with which the dihydroresorcin is brought in contact. As a result, in the series of reactions which give rise to 1 : 1 : 2-trimethylcyclohexan-3-one, both 1 : 1 : 2-trimethylcyclohexan-3-ol and 1 : 1 : 2-trimethylcyclohexan-5-ol are formed, both of which alcohols are capable of existing in *cis* and *trans* modifications, but so far only the *trans* form of 1 : 1 : 2-trimethylcyclohexan-3-ol has been isolated. These alcohols give rise to the corresponding ketones on oxidation, but here again only 1 : 1 : 2-trimethylcyclohexan-3-one has been isolated in a pure condition. Further experiments are now in progress.

THE INFLUENCE OF CARBON AND OTHER ELEMENTS ON THE CORROSION OF STEEL.*

THE subject of the corrosion of iron and steel is one that is rapidly engaging considerable attention in the metallurgical world, the researches of Friend, Cushman, Walker, Longmuir, and others having brought it deservedly into considerable prominence. Despite the fact, however, that the modern metallurgy of iron and steel largely centres about the influence of various alloying elements upon its physical and mechanical properties, no reliable data are available as to the influence exerted by them upon its corrodibility. In view of the absence of such data regarding the influence of carbon, in gradually ascending percentages, upon the corrodibility of iron, and especially in view of the fundamental importance of carbon as an iron-alloying element, the Committee have confined their attentions solely, during the past year, to the investigation of the influence exerted by this element upon the corrodibility of iron.

An attempt was made by Andrews to obtain some data regarding this question, and his results were published in 1885 in a paper on "The Corrosion of Metals during Long Exposure in Sea-water" (*Proc. Inst. Civil Engs.*, lxxii., 281)—one of a series of brilliant and systematic researches on corrosion which are unfortunately not so well known as they deserve to be. His ascending carbon series, however, included such widely diverse materials as wrought iron, Siemens and Bessemer steels, and also crucible cast steels, in which the percentages of Si and Mn vary considerably, rising as high as 0.4 per cent and 1.3 per cent respectively, whilst the S and P in some cases respectively reach such abnormal figures as 0.12 per cent and 0.27 per cent each. The values given by such a series can hardly be relied upon as being indicative of the influence of carbon alone upon the corrodibility of iron.

A series of pure iron-carbon alloys have therefore been obtained by the Committee in order not only to indicate the influence of carbon upon the corrodibility and other properties of iron, but to serve also as a base line from which the influence of other elements upon the corrodibility of steel may be determined in future researches. These pure iron-carbon alloys were prepared by the coke crucible process in the Metallurgical Department of Sheffield University, the materials employed being Swedish bar-iron and charcoal, this method having been found to give the purest iron-carbon alloys obtainable. Six such alloys have been employed, ranging from 0.10 per cent to 0.96 per cent carbon, and the microscopic examination in the rolled condition showed the distribution of the micro-constituents in these steels to be remarkably even throughout the whole of the series. It is also important to note that, despite careful search, no traces were found of manganese sulphide, the powerfully electro-positive nature of which tends to cause serious electrolytic action when present in steel, thus materially increasing the corrodibility.

The determinations of the corrodibility and other properties of these steels have been carried out in several states of heat treatment, which have been designed to resolve the pearlite into the principal varieties in which it usually exists in carbon steels, viz. :—(a) Diffused, (b) laminated, and (c) emulsified, and also into hardenite, which is the essential constituent of hardened carbon steels. The treatments employed were (1) as rolled, (2) normalised, (3) annealed, (4) and (5) hardened and tempered at (a) 400° C. and (3) 500° C., (6) hardened.

Determination of Simple Corrosion in Sea-water.

The relative corrodibilities of these steels in all states of treatment have been measured by immersing polished cylindrical bars of the various specimens ($\frac{1}{4}$ inches long $\times$ $\frac{3}{8}$

* Report of the Committee, consisting of Prof. J. O. Arnold (Chairman), Dr. W. E. S. Turner (Secretary), Prof. W. P. Wynne, Prof. A. McWilliam, Mr. C. Chappell, and Mr. F. Hodson. Read before the British Association (Section B), Portsmouth Meeting, 1911.

inches dia.), each separately in 700 cc. sea-water for a period of thirteen weeks, the loss in weight per cent during this period being determined.

The results obtained, as plotted in Fig. 1, indicate that the carbon exerts two types of influence upon the corrodibility, dependent upon the condition of the carbide in the steel. In the rolled, normalised, and annealed specimens, in which the carbide (as shown by microscopic examination) exists entirely either as the diffused normal variety, or as the laminated variety of pearlite, the corrodibility rises to a maximum at saturation-point (0.89 per cent carbon), and then decreases upon the appearance of cementite in the steel. The rise in corrodibility in such steels with increase of carbon from 0.10 per cent to 0.89 per cent is not regular, but is much more rapid in the range 0.3 per cent to 0.89

being mainly of the diffused variety, take up an intermediate position. This indicates that the finer the state of division of the carbide in the pearlite, the greater is the liability to corrosion when immersed in sea-water—a conclusion which is in complete accordance with the electrolytic theory advanced by Cushman (*Journ. Iron and Steel Inst.*, 1909, i., 33) and Walker (*Journ. Iron and Steel Inst.*, 1909, i., 69). This is also supported by the fact that in the case of tempered steels a rise in the tempering temperature from 400° C. to 500° C. produces a marked decrease in the corrodibility, this, no doubt, being due to the slight decrease in the fineness of division of the pearlite which is produced by the rise in tempering temperature. The conversion of the pearlite into hardenite is accompanied by a very considerable rise in corrodibility,

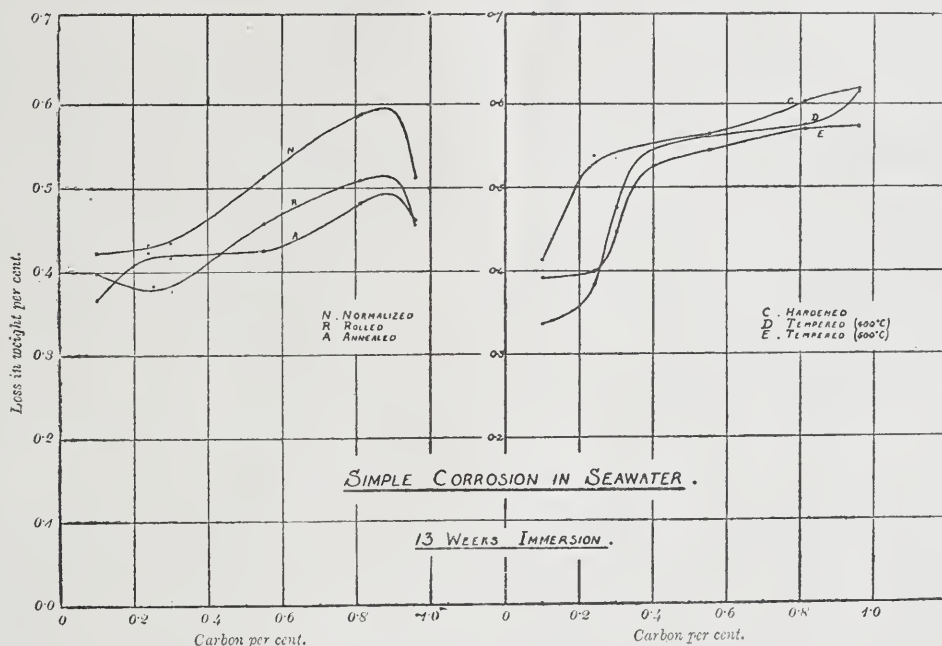


FIG. 1.

per cent carbon than in the low carbon range 0.10 per cent to 0.3 per cent carbon.

In the hardened and tempered specimens, however, in which the carbide has been converted respectively either to hardenite or the emulsified variety of pearlite, it has been found that the corrodibility rises continuously from 0.10 per cent to 0.96 per cent carbon, no maximum being observed at the saturation-point. The proportional increase of corrodibility in these steels with rise of carbon per cent is very rapid up to about 0.25 per cent carbon in the case of the hardened steels, and about 0.40 per cent carbon in the tempered specimens. After these points the rate of increase of corrodibility with rise of carbon per cent is small but regular up to 0.96 per cent carbon, being in this respect the reverse of that found in the type first described.

The state of division of the carbide in the pearlite is found to exert very considerable influence on the rate of corrosion of iron-carbon alloys. In general, the annealed steels, in which the carbide exists entirely in the laminated condition, show a minimum corrodibility, whilst the tempered steels containing the carbide as the emulsified variety show a maximum corrodibility—except in the very low carbon steels. The normalised steels, moreover, in which the carbide is in an intermediate state of division,

the hardened steels corroding more rapidly than any of the unhardened or tempered steels.

Careful examination of the deposits on the corroded bars on removing them from the sea-water shows the rust deposit to be made up of two different types. These may be briefly described as:—

(a) Light brown deposit, flocculent and easily removed, forming an even coating over the whole of the exterior of the rust deposit.

(b) A deposit of a bluish black colour, somewhat greenish in some cases, underlying the previous mentioned deposit. This is mainly found at the lower end of the bars, to which it is usually somewhat firmly adherent. In the case of the hardened and tempered specimens a thin easily removed layer of a similar colour is found covering the whole of the bar underneath deposit (a), in addition to the firmly adherent deposit at the lower end. Whether this deposit is merely a form of deposit (b), or whether it is really a chemically different type of deposit of the same colour, is not known. A detailed examination of these respective deposits might probably throw considerable light on the phenomena involved in the corrosion of steel.

To be continued.

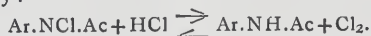
THE TRANSFORMATION OF AROMATIC
NITROAMINES AND ALLIED SUBSTANCES,
AND ITS RELATION TO SUBSTITUTION
IN BENZENE DERIVATIVES.*

*Transformations of Chloro- and Bromo-amines into
Halogenanilides.*

IN last year's Report the following conclusions were reached :—

1. The chlorination and bromination of anilides is a direct process, and does not take place by way of the chloro- or bromo-amines. These substances are by-products.

2. The conversion of a chloroamine into the isomeric chloroanilide can only take place in the presence of hydrogen chloride. This acid and the chloroamine react reversibly :—



The anilide and chlorine can then react directly, forming chloranilide.

Hydrogen bromide (and hydrogen iodide) react similarly, for example, in a suitable medium :—



Bromination of the anilide and not chlorination now ensues.

3. When chlorine reacts with an anilide, two very rapid changes occur side by side, (a) the formation of a chloroamine, Ar.NCl.Ac , and hydrogen chloride, N-chlorination; (b) the formation of a chloroanilide, ClAr.NH.Ac , and hydrogen chloride, C-chlorination.

4. The existence of a complex, Ar.NH.AcCl_2 , as an intermediary in these reactions was discussed. Its relations are shown in the scheme :—



Although its existence is not excluded by the results, it was shown that such a complex must have very different properties in the case of different anilides; as the composition of the medium is changed, the concentration of the complex must vary greatly: the speed of the transformation of the complex into chloroanilides must depend not only on the constitution of the anilide, but also on the constitution of the medium.

To avoid such a number of arbitrary assumptions it seems at least simpler to regard chlorination as occurring directly, and not by way of such a complex.

The Velocity of Chlorination of Anilides (Trans. Chem. Soc., 1911, xcix., 1369).

(With HAROLD KING, M.Sc.).

The speed of the chlorination of anilides is being investigated with the object of ascertaining the effect of the nature, the number, and the position of various substituents, and the effect of acyl groups on the reaction.

Owing to the simultaneous formation of chloroamines, Ar.NCl.Ac and C-chloro-derivatives, ClAr.NH.Ac , in dilute acetic acid, it is obviously simplest to measure the speed of the formation of the latter, in glacial acetic acid, when the former does not occur.

In glacial acetic acid, the reaction of chlorine and anilide is of the second order. It appears to be quite simple in character; no disturbing side reactions are observed, and the values of the velocity coefficients are remarkably constant throughout the reaction.

As the change proceeds hydrogen chloride appears in the solution. Control experiments have shown that even

when as much as 8-grms. molecular proportions of the acid are added, the velocity of chlorination is not affected. This fact offers a marked contrast to bromine in the presence of hydrogen bromide. Addition of hydrogen bromide arrests the bromination of anilides owing to the formation of hydrogen perbromide, HBr_3 (compare Report, 1910).

The following table gives the value of the velocity coefficient, k_{ij} , temperature 16° , concentrations in gm. molecules per litre, and time in minutes :—

	k_{ij} .
Formanilide	4.95
Acetanilide	40
Propionanilide	72
Butyranilide	64.5
isoValeranilide	57
Stearanilide	6
Oxanilide	2
Benzanilide	42
Aceto-o-aniside	60
Aceto-p-aniside	57
Aceto-o-phenetide	90
Aceto-p-phenetide	85
Aceto-o-toluidide	9
Aceto-p-toluidide	77
Benzo-o-toluidide	5.7
Benzo-p-toluidide	70
Aceto-m-xylidide	9
Aceto-ψ-cumidide	630
Aceto-α-naphthalide	550
Aceto-β-naphthalide	∞
Formo-α-naphthalide	365
o-Chloroacetanilide	0.073
p-Chloroacetanilide	0.21
p-Chlorobenzanilide	0.16

Relation between the Nature of the Acyl Groups, and the Proportion of Ortho- and Para-chloro-derivatives formed in Chlorinating Acylanilides (Trans. Chem. Soc., 1911, xcix., 1377).

(With HAROLD KING).

We have extended the experiments begun by Mr. W. J. Jones (*Trans. Chem. Soc.*, 1909, xcv., 1056) on the estimation of the proportion of o- and p-chloro-derivatives which are formed in the chlorination of acylanilides. The results so far obtained are shown in the table. The acyl group is found to have a very powerful influence. Other circumstances, media, temperature, and concentration, have little effect on the proportion, but the production of a dichloro-derivative is more pronounced in other media than dilute acetic acid.

The numbers represent the percentage of the anilide chlorinated, found in the product in one or other form.

Anilide.	p-Chloro-anilide.	o-Chloro-anilide.	Ratio: o-Chloro-anilide p-Chloro-anilide.	2:4-Dichloro-anilide.	Un-changed anilide.
Acetanilide ..	51	44	0.89/1	1.2	1.2
Propionanilide ..	64	26	0.4/1	3.2	3.2
Stearanilide ..	69.5	20.8	0.3/1	2.2	2.2
Benzanilide ..	65.5	11.2	0.17/1	11.1	9.2
Formanilide ..	62	3.0	0.048/1	—	—

Obviously the chlorination of acetanilide is the best method of preparing o-chloroaniline.

An Application of the Reaction between Chloroamines and Hydrogen Chloride as a Method of Chlorinating Anilines and Phenols (Trans. Chem. Soc., 1911, xcix., 1185).

(With HAROLD KING).

The fact that chloroamines and hydrogen chloride react quantitatively in glacial acetic acid, producing anilide and chlorine, gives a very effective method of chlorinating such

* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, Dr. A. Lapworth, and Dr. J. T. Hewitt. Read before the British Association (Section B), Portsmouth Meeting, 1911.

anilides and phenols as are particularly susceptible of oxidation, or by the usual methods yield di- or poly-chloro-derivatives.

Molecular proportions of the substance to be chlorinated and a chloroamine, for example, that derived from 2:4-dichloroacetanilide or *p*-nitroacetanilide, are mixed in glacial acetic acid solution, and some small proportion of hydrogen chloride, one-hundredth to one-twentieth grm. molecular proportion, added. From the reaction between the chloroamine and the hydrogen chloride, chlorine is formed in amount molecularly equivalent to the hydrogen chloride used. The chlorine in its turn attacks the substance to be chlorinated, forming at the same time an equivalent of hydrogen chloride. Chlorine is again regenerated, and hence it is thus maintained at a constant low concentration, fixed by the amount of hydrogen chloride originally introduced, through the greater part of the reaction.

In this way 5-chloro-*m*-xylylidine, 6-chloro- ψ cumidine, 5-chloro-*o*-anisidine, 5-chloro-*p*-anisidine, 5-chloro-*o*-phenetidine, and 5-chloro-*m*-xyleneol have been for the first time prepared. Further, Mr. King has been able to chlorinate α -naphthol directly without any oxidation. Owing to the fact, however, that the speeds of interaction of α -naphthol and 4-chloro- α -naphthol and chlorine are of similar magnitude, much 2:4-dichloro- α -naphthol is formed, and hence an equivalent quantity of α -naphthol remains unchanged. α -Naphthol can be quantitatively converted into 2:4-dichloronaphthol by this method.

Formation of Nitroamines. (With Miss M. G. EDWARDS).

There is no easier way of preparing certain nitroamino-benzenes than by treatment of the aniline in acetic acid solution with a mixture of acetic anhydride and nitric acid in the same solvent. With di-ortho-(negatively)-substituted anilines the yield of nitroamine is quantitative. With other anilines the acetyl derivative is formed simultaneously, owing to the more rapid interaction of acetic anhydride with anilines in which an ortho-position is unoccupied, or not occupied by a negative group. The proportion of nitroamine to acetyl derivative can be to a certain extent regulated by variation of the concentrations of the acetic anhydride and nitric acid.

It appears to be generally thought that the formation of the nitroamine is due to the dehydration of the aniline nitrate. There is, however, much evidence that such is not the case.

1. It was shown by Smith and Orton (*Trans. Chem. Soc.*, 1908 and 1909) that all acids, except nitric acid, acted as powerful accelerators of acetylation of anilines by acetic anhydride. There is no formation of the anilide of the acid of the type corresponding to the nitroamine.

2. Measurements have been made of the rate of the formation of nitroamines by this method. In one series of experiments the anhydride is added to a mixture of aniline and nitric acid in acetic acid; a relatively slow regular formation of nitroamine follows. In other series the anhydride and nitric acid are mixed in acetic acid, and then added to the solution of the aniline; a very rapid formation of the nitroamine takes place, the speed, however, falling off after about half the reaction is over.

This result obviously suggests that a compound of acetic anhydride and the nitric acid is the nitrating agent. In the second series it can be formed and reach a high concentration before it is brought in contact with the aniline. This compound may be the compound prepared by Pictet, $(\text{CH}_3\text{CO})_2\text{N}(\text{OH})_3$ (*Centrablatt*, 1903, ii., 1109), or even acetyl nitrate.

3. A remarkable confirmation of this view is found in some experiments which have been recently carried out on the hydrolysis of acetic anhydride (with Miss M. Jones). The anhydride was dissolved in a large excess of acetic acid, which contains a small proportion of water, 0.12 to 0.2 per cent. The hydrolysis of acetic anhydride in this medium is extremely slow at the ordinary tempera-

ture. In the presence of small proportions ($\frac{1}{2}$ to $\frac{1}{4}$ grm. molecular proportion) of all mineral acids, with the exception of nitric acid, an extremely rapid hydrolysis occurs. With nitric acid there is no acceleration, but even a retardation of the hydrolysis. In dilute (80 per cent) acetic acid, there is no difference between nitric acid and other acids.

There seems little doubt then that nitric acid and acetic anhydride, even when largely diluted with acetic acid, very rapidly react or combine. On the one hand, this compound attacks anilines forming nitroamines, and not acetyl derivatives, and on the other hand this compound does not react with water more rapidly than acetic anhydride itself.

The Committee desire to be re-appointed for the coming year, and ask for a grant of £15.

PLEUROTUS CRETACEUS, AN INDIAN EDIBLE MUSHROOM.

By DAVID HOOPER, Calcutta.

DURING the recent examination of several Indian food-stuffs, more especially for their phosphorus content, I was struck with the peculiar composition of an edible mushroom largely used in Northern India. Several fresh and dried species of fungi are eaten in the country, but few of them have been determined botanically. The one under enquiry has, however, been described by Mr. Masser, of Kew Gardens, in the "Kew Bulletin," 1899, p. 165. The descriptive note is as follows:—"Pleurotus *cretaceus*, Masser, a very remarkable fungus, entirely creamy white. Very rigid when dry, and looking exactly like a plaster of Paris model. Allied to *P. sapidus*, Kalchbr." Dr. Watt's note accompanying the specimen is as follows:—"It comes from Peshawar, where it is known as 'Dhingri.' It is said to be sold by the shopmen much broken. The average price at which it is sold is Rs. 2.8 per seer. Before cooking it is soaked in fresh water for about eight hours. It then swells and become pulpy. It is sent as a rarity in presents to friends all over India.

The dried fungus was reduced to powder, and analysed in the usual way as a foodstuff. Its proximate composition is here set out:—

Moisture	12.25
Albumenoids (containing nitrogen, 3.40)	21.25
Carbohydrates	54.70
Crude fibre	3.05
Ash (containing phosphoric anhydride, 1.85)	8.75

100,000

The comparatively large amount of phosphorus in the ash caused me to examine a further sample quantitatively. The ash is shown to consist largely of alkaline carbonates and phosphates.

Calcium carbonate	0.36
Magnesium carbonate	0.21
Potassium carbonate	0.27
Sodium carbonate	2.14
Sodium phosphate	4.32
Sodium sulphate	trace
Silica and sand	0.20
	7.50

Hydrogenation of Carvone.—G. Vavon.—The hydrogenation of carvone in presence of platinum takes place in three stages. In the first stage the carvone is transformed into carvotanacetone; next *l*-tetrahydrocarvone is formed, and finally, if hydrogenation is allowed to proceed, carvomenthol is obtained. This method of reduction of the ketone function can be applied to many ketones and aldehydes, which are thus converted into the corresponding alcohols.—*Comptes Rendus*, cxiii., No. 1.

A STUDY ON THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.*

THE CHIEF SOURCES OF ERROR IN THE METHOD.

By E. M. CHAMOT, D. S. PRATT, and H. W. REDFIELD.

SOON after the method, known also as the Grandval and Lajoux or Sprengel method, became known and quite generally adopted by water analysts, perplexing variations in results and peculiarities in the behaviour of the reagents used were reported by many; but it is only within comparatively recent years that a thorough systematic study of the method has been made, the earlier work being abortive because of incomplete knowledge of the composition of the reagent and of the composition of the coloured reaction product upon which the entire method depends. The evolution and improvement of the method has already been summarised in two preceding papers and need not here be again discussed (Chamot and Pratt, *Journ. Am. Chem. Soc.*, xxxi., 922; xxxii., 630).

For the purposes of study and discussion the chief errors which may affect the results as obtained by the method as now in use may be conveniently grouped under the following heads.

- I. Errors resulting from—
 - a. The use at different times of sulphonic acids of varying composition.
 - b. The use of reagents of different ages and therefore of changing composition.
- II. Errors resulting from the use at different times of varying volumes of reagent.
- III. Errors resulting from variable time of contact between reagent and water residue.
- IV. Errors due to differences in the temperature of the water residue and standard when the reagent is applied or those resulting from a great rise in temperature when the alkali is added.
- V. Errors due to variations in the alkali employed.
- VI. Errors due to the presence of organic matter.
- VII. Errors due to losses through evaporation.
- VIII. Errors due to the presence of carbonates.
- IX. Errors due to the presence of chlorides in the residue.
- X. Errors due to the presence of iron.
- XI. Errors due to the presence of other forms of interfering inorganic compounds not covered above.

The attention of water analysts has been called to most of these sources of error by many previous investigators, nevertheless it has been thought best to again review all these difficulties, and it is the purpose of this paper to discuss in a brief manner these sources of error and point out the shortcomings of the phenolsulphonic acid method as now practised, and to suggest what appears to be a marked improvement in the process whereby it is possible to eliminate the worst of the troubles.

For convenience the sources of error above listed will be taken up for discussion in the order given.

I. (a), (b). Errors Due to the Variable Composition of the Reagent.

The fact that the composition and method of preparing the sulphonic acid reagent affected the delicacy of the method and influenced the intensity and shade of the yellow colour of the reaction products appears to have been early recognised by analysts, since the literature of this method contains many directions for making reagents in greatly varying proportions of phenol and sulphuric acid and in the subsequent treatment of the mixture.

These reagents fall into four broad classes.

- A. Those made by mixing phenol and concentrated sulphuric acid at ordinary temperatures (Lombard, *Bull. Soc. Chim.*, 1909, [4], v., 1092).
- B. Those made by mixing phenol and concentrated sulphuric acid to which a little water has been added (Smith, *Analyst*, 1885, x., 199; Girard and Lajoux, *Comptes Rendus*, 1865, ci., 62; Rideal, *CHEMICAL NEWS*, 1889, lx., 261).
- C. Those made by mixing phenol and concentrated sulphuric acid and adding thereto a little concentrated hydrochloric acid (Johnson, *CHEMICAL NEWS*, 1890, lxi., 15; Farcy, *Bull. Soc. Chim.*, 1909, [4], v., 1088).
- D. Those made by heating a mixture of phenol and concentrated sulphuric acid (Gill, *Tech. Quart.*, 1894, vii., 55; *Journ. Am. Chem. Soc.*, 1894, xvi., 122).

Until the compound giving the yellow colour in the alkaline solution had been isolated and purified, great difficulty was experienced in studying the errors of the method, as no satisfactory and reliable standards could be prepared which would not themselves be subject to part of these same sources of error. The colour top, colour wheel, and tintometer suggested themselves, but proved impracticable. As soon, however, as the pure tripotassium nitrophenoldisulphonate was obtained, a means of preparing standards of exactness and permanence became available. It was now possible to weigh out portions of this compound containing known amounts of nitrogen and prepare a series of standards whose colour was found to remain unchanged for many months. Moreover, these standards could be diluted with computed volumes of water and still show the correct colour tint and intensity in a colorimeter corresponding to the reduced nitric nitrogen content.

The importance of the discovery of this method for the preparation of invariable standards made from the actual colour compound will be appreciated by all readers. Directions for preparing tripotassium nitrophenoldisulphonate will be found given in our fourth paper. In order that the results of colorimeter reading should be as free as possible from the personal equation, in all the work described below, the colours were read in turn by two and usually three observers, absolutely independently and with the key to the strengths of solutions or methods being investigated in the hands of one observer only. It was thus possible to eliminate bias and preformed opinions.

The reagents falling under Class A may vary greatly in composition, depending upon the proportions of phenol and sulphuric acid, upon the way in which the materials are mixed, and upon the age of the reagent. In sulphonic acid reagents of this type it is possible to have the ortho-sulphonic acid remain in the mixture only when no great excess of sulphuric acid is used; otherwise the mixture as first made contains a little ortho, much para, and some disulphonic acids. Moreover, the amount of the disulphonic acid increases with the age of the reagent. These facts we have been able to prove by analyses of practically all the types of reagents by the methods already described by us in papers I. and II. By way of illustration the most recently described reagent, that of Lombard (*Bull. Soc. Chim.*, 1909, [4], v., 1092), is made by mixing phenol and concentrated sulphuric acid at room temperature. When freshly prepared this was found to contain large amounts of mono acids. Nitrate-containing water residues treated with this fresh reagent, and made alkaline in the usual manner, showed in the colorimeter greenish tints, as was to be expected, instead of pure yellows. After ten days the sulphonation had progressed so that nearly all the acid was now phenoldisulphonic acid. Greenish colours in the final product were now obtained only when the residue and reagent were warm. After standing six months little further change could be detected.

It is evident that these variations in the composition of reagents of Class A must introduce decided errors where results of analyses made at one time are to be compared

* From the *Journal of the American Chemical Society*, xxiii., No. 3.

with those obtained at another time, inasmuch as there is both a variation in the final products of the reaction and a variation in the sensitiveness of the reagent. This is especially true if permanent standards are employed. Reagents of Class A type must be allowed to stand some time before use. Since, however, the rate of sulphonation is indefinite and not easily measured, there is no certainty when an equilibrium has been reached. Moreover, it has been shown that the orthosulphonic acid gives greens in the final product in the cold (Paper I., *loc. cit.*), the intensity of the green being proportional to the amount of ortho acid present, thus giving rise to great variations in the colorimeter readings and rendering comparisons with results obtained with different reagents impossible.

The parasulphonic acid, on the other hand, gives final green colours only when warmed in contact with the nitrate. But it must be remembered that in this contact, unless special precautions are taken, sufficient heat is generated to nitrify the para acid; moreover, when water is added to dilute the reagent after contact a marked rise in temperature again results, which is further increased when the alkali is added to develop the colour. When much para acid is present, green tints must thus invariably result unless the water residue is kept in a freezing mixture during the addition of reagent, water, and alkali. The greater the rise in temperature the more intense is the greenish tint. Thus here too a decided error is introduced.

Reagents falling in Class B and Class C have the same faults as those of Class A. It follows, therefore, that any sulphonic acid reagent of greatly varying composition must be regarded as undesirable, and that the more stable the reagent is and the smaller the number of component sulphonic acids the better and more reliable will be the results obtained.

Since the final yellow product whose colour intensity is measured, in arriving at the amount of nitric nitrogen present in a sample of water, is due to an alkali salt of nitrophenoldisulphonic acid (Chamot and Pratt, *Journ. Am. Chem. Soc.*, xxxii., 630), it follows that reagents of Class D are best and most reliable. This was long ago shown by Gill (*Tech. Quart.*, 1894, vii., 55; *Journ. Am. Chem. Soc.*, 1894, xvi., 122, 193). Heating the phenol with the concentrated acid accomplishes, in a short time, a degree of sulphonation which only very long standing could bring about.

Gill's reagent having been found to be the best of those proposed, and having been adopted by the American Public Health Association, it has been termed the "standard" reagent in the preceding papers and has been selected in the present instance for the study of the sources of error given above. In his paper describing his method for the preparation of the disulphonic acid reagent Gill stated no reasons why the ratio of 3 grms. of phenol to 37 grms. of sulphuric acid was adopted. It was therefore first necessary to ascertain the proper proportion of phenol and sulphuric acid in reagents which could be prepared by the heating method. With this end in view mixtures were made varying in composition from 1 gm. molecule of phenol with 1—16 gm. molecules of sulphuric acid. All were heated for six hours at 100° in the usual manner. It was found that the best and clearest yellow colours were obtained when the mixture contained 12 or more gm. molecules of sulphuric acid. This proportion is that of Gill's reagent, and fully confirms his work. Moreover, it was further found that reagents containing less sulphuric acid would solidify after standing several days in a cool place owing to crystallisation of the sulphonic acid.

The Gill or standard reagent, however, still contains sufficient monopara acid to yield greenish tints if the reagent is poured upon a warm nitrate-containing residue, or if there is a marked rise in temperature either upon dilution with water or upon the addition of alkali, thus introducing marked errors at times and of very different degrees. The standard reagent is therefore not a safe or satisfactory one, particularly if permanent standards are employed. The

conversion of all of the phenol into the disulphonic acid by the method described later, with the elimination of the small quantity of mono acid still present in the standard reagent, removes at once these sources of difficulty.

II. Errors Due to Variable Volumes of Reagent.

It has been quite generally assumed that, providing volume of the sulphonic acid reagent sufficient to cover the water residue is used, it makes little difference whether this volume be much or little within certain narrow limits although Leffmann appears to have recognised the importance of using exactly equivalent volumes on the known and unknown nitrate residue ("Examination of Water," p. 52). This assumption that the colour is independent of the volume of reagent used is not warranted, however, the facts being that the final colour is actually greatly influenced by the volume of the reagent employed, the intensity increasing with the volume, and when more than 4 or 5 cc. of the standard reagent are used, greenish colours appear in the final alkaline liquid. Murky tints almost impossible to match in a colorimeter are also often produced even when no green is discernible. With volumes of reagent in excess of 5 cc. a large amount of inorganic sulphate usually separates, obscuring sufficient of the yellow compound to necessitate dilution beyond the capacity of the colorimeter cylinders commonly employed.

The following table shows the average apparent increase of nitrate due to increasing volumes of standard reagent used, the lowest volume being here assumed for purposes of comparison as the correct value.

Cubic centimetres of standard reagent used.	Water residue with N indicated in parts per million.				
	2 parts.	4 parts.	6 parts.	8 parts.	10 parts.
1 cc. taken as ..	2	4	6	8	10
2 cc. equivalent to	2.3	4.4	6.6	8.8	11.1
3 cc. equivalent to	2.7	5.1	7.7	10.0 (b)	13.1
4 cc. equivalent to	3.2	5.6 (a)	8.2	11.0 (b)	14.2 (b)
5 cc. equivalent to	4	6.4 (a)	9.8 (a)	12.9 (c)	15.5 (c)

(a) Murky tints difficult to compare with the 1 cc. colour.
(b) Greenish tint. (c) Very green.

These results clearly show that there is a very decided error unless the standard reagent is very carefully measured and exactly the same volume is employed in treating both the known nitrate containing residue and that of the sample of water being examined. Practically identical results as to intensity are obtained when the reagent contains no mono acids, except that in this case neither murky nor green tints develop.

The commonly accepted procedure has been to employ 2 cc. of sulphonic acid. This volume gives satisfactory colours of sufficient intensity and free from murky or greenish tints, and there is therefore no good reason to depart from this volume now used by common consent, but it must be borne in mind that this volume must be carefully measured if accurate results are required.

Thinking that the very marked increase in colour resulting when large volumes of reagent are used might possibly be due in part to ionic concentration and to variation in dissociation, runs were made using a variety of radical combinations, *e.g.*, sodium, potassium, ammonium, magnesium, and calcium nitrates as sources of nitric nitrogen. The concentration of the sulphate ions was also varied by the addition of potassium sulphate. In all cases the final colours were the same both in tint and intensity.

Since the green tints and colours are due to nitrification of monosulphonic acids, and since it had already been ascertained that the standard reagent gave green tints only when warmed with nitrates, it appeared probable that the darker colours and changes in tint observed with volumes of reagent greater than 2 cc. resulted from the rise of temperature that naturally followed when stronger acid was neutralised. This heat, curiously enough, seems to account for the changes in colour intensity shown in the table,

The colour obtained by using 4 cc. of standard reagent is almost exactly matched if to 2 cc. of reagent, 2 cc. of concentrated sulphuric acid is added. Moreover, if 2 cc. of reagent be used, water added, and the whole kept boiling while the alkali is added, it is found that the resulting yellow colour is darker than that obtained in the usual manner; e.g., with residues containing 10 parts of nitrogen as nitrate per million the following results were obtained:—

- 2 cc. of reagent taken as = 10 parts N.
2 cc. of reagent + 2 cc. of H_2SO_4 = 13.4 parts N.
2 cc. of reagent neutralised hot = 11.3 parts N.

If the elevation of temperature causes the apparent increase in the nitrate content, the reverse should hold true. This has been confirmed experimentally by treating the cold residue with the standard reagent, diluting with cold water, and keeping at 0° by means of cracked ice while the cooled alkali was slowly added. It was found that in all cases the final colours obtained were of less intensity than when the usual practice was followed, the apparent difference being less by 0.2–0.4 of a part per million according to the volumes of reagent used. This discrepancy is here again due to the presence of mono acids, since with reagents containing only the disulphonic acid, equivalent volumes of reagent give identical final colour intensities irrespective of whether cooled with ice or not.

III. Errors Resulting from Variable Time of Contact between Reagent and Residue being Treated.

In a reaction involving the introduction of nitro groups into a sulphonic acid an appreciable length of time is necessary in order that the final product shall show the full content of nitrogen. In order that the minimum time might be ascertained a number of experiments were performed, all of which showed that the reagent and residue should remain in contact at least two minutes after the complete covering of the residue. By way of illustration it is necessary to cite only one of the series of trials made. In this, residues containing 10 parts per million of nitrogen as nitrate were compared with the pure tripotassium nitrophenoldisulphonate standards.

Time of contact.	Parts N found.
15 seconds	8.8
30 seconds	8.9
1 minute	9.2
2 minutes	10
5 minutes	10
10 minutes	10
19 hours	10

In obtaining contact between reagent and all particles of residue the best practice is to mix the two with a glass rod, crushing all particles that may be found. With waters high in total solids containing little nitrate it is essential that the particles be crushed and that a contact of over two minutes be allowed.

IV. Errors Due to Differences in the Temperature of the Residue when the Reagent is Applied.

Richards and Hollings have pointed out that the final colour varied greatly with the temperature at which the reagent acted upon the residue (*Soc. Chem. Ind.*, 1903, xxii., 616). The usual procedure in America has been to allow the residues obtained by evaporation on the water-bath to cool to room temperature before applying the reagent. It has already been shown in the present paper that the final colour is greatly intensified by temperature. With reagents containing monosulphonic acids all sorts of variations in intensity and tint are obtained if the reagent be applied to a hot residue, and very serious errors result if standard nitrate and water residue are not treated exactly alike as to temperature. Failure to observe this precaution leads to enormous errors. Should the reagent be applied at once to the residue upon its removal from the water-

bath, so much green appears in the final product as to render impossible a comparison with a nitrate standard prepared at room temperature. The greater the proportion of monosulphonic acids present the greater will be the deviation from the yellow colour of the nitrate standard.

If a reagent consisting wholly of disulphonic acid be employed, there is no change whatsoever in colour intensity caused by heating, and no green tints appear. It has been possible to heat reagents of this type for over three hours on the water-bath in contact with nitrate residues and still obtain the same brilliant yellow as that of the permanent nitrate standard.

(To be continued).

NOTICES OF BOOKS.

The Technology of Bread-making. By WILLIAM JAGO, F.I.C., F.C.S., and WILLIAM C. JAGO. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1911. (21s. net).

THE outstanding feature of this work is its comprehensiveness, and it is impossible to think of any information which the confectioner or the miller could require and could not readily get from it. The chemistry of bread is first fully treated, the constituents of wheat being described individually and in detail. Much attention is paid to fermentation, and full accounts are given of the technical researches performed by the authors and by other chemists which bear on bread fermentation. The designing of bakeries and bread-making machinery is given full consideration, and many questions of commercial importance, such as the valuation of flour, the weighing of bread, the relative nutritive values of different kinds of flours, are discussed. The chemical analysis of flour and yeast are included, and the results of a very large number of analyses are collected, while the last chapter gives some account of the chemistry of confectioner's raw materials. As a standard work for the technical student as well as for the practical man the book will be most serviceable, and in every respect is well-balanced and up-to-date.

Essays in Historical Chemistry. By Sir EDWARD THORPE, C.B., LL.D., F.R.S. London: Macmillan and Co., Ltd. 1911. (12s. net).

SOME of the lectures which are contained in this book were delivered nearly forty years ago, others are of much more recent date, but all are marked by the same gift for graphic description and illuminating criticism and comment which is the special characteristic of the author. One or two essays are included among the lectures, which were delivered before audiences of various classes, and hence differ widely in style. The lectures were mostly biographical, and are here arranged in historical sequence; the first deals with the life and work of Robert Boyle, and the last with Julius Thomsen, and those on the later chemists will be read with particular interest by students and teachers, for it is not always easy to find a fair unbiased estimate of the value and influence of the contributions of modern workers to the advancement of the science. The last three lectures deal respectively with the Rise and Development of Synthetical Chemistry, the Progress of Chemistry in Great Britain and Ireland during the Nineteenth Century, and the Development of the Chemical Arts during the Reign of Queen Victoria, and although to a certain extent they overlap, the author has so much that is interesting to tell his readers that no one will be wearied by reading them all.

Nitrocellulose Industry. By EDWARD CHAUNCEY WORDEN, Ph.C., M.A., F.C.S. Two Volumes. London: Constable and Co., Ltd. 1911. (42s. net, two vols.).

THE applications of the derivatives of cellulose in the "peaceful arts" have recently been wonderfully extended, and the magnitude of the nitrocellulose industry will prob-

ably come as a surprise to many purchasers of this book. After introductory chapters on the chemistry and technology of cellulose and the process of nitration, the chemistry of solvents of the nitrates is fully treated, and the applications of pyroxilin solutions in the production of lacquers, imitation leathers, &c., are described in lengthy and very complete chapters. The preparations and uses of celluloid occupies a large part of the second volume, in which there is also a chapter on the outlines of the chemistry of smokeless powders. The book is well indexed, and all the patents of the United States, England, Germany, and other countries dealing with the nitrocellulose industries are tabulated.

Modern Industrial Chemistry. From the German of H. BLÜCHER. Translated by J. P. MILLINGTON, M.A. (Cantab.), B.Sc. (Wales). London: The Gresham Publishing Company. 1911. (30s. net).

THERE is little doubt but that this book will be found as useful to English chemists, engineers, and manufacturers as the original has been in Germany. In many respects it partakes of the nature of a technical lexicon, and the alphabetical arrangement of its contents is a feature which will appeal to busy men who require a work of reference. All the important products of the chemical industries are included, and short descriptions are given of their preparation, uses, &c., with some notes on the chemistry of them and their physical properties; a good many pharmaceutical preparations are included, and the book is very complete in this respect. Patent literature is also carefully abstracted, and a good choice has been made of those patents selected for more detailed treatment. A few conversion tables are given in an appendix and some tables for calculating the results of analyses.

Die Neue Welt der Flüssigen Kristalle. ("The New World of Liquid Crystals"). By O. LEHMANN. Leipzig: Akademische Verlagsgesellschaft. 1911. (M. 12).

THE engrossing subject of liquid crystals, which may indeed be said to belong to a new world, is delightfully treated in this book by the physicist who has studied it more thoroughly and has a fuller and more complete knowledge of it than any other man now living. The book consists of short chapters, which are beautifully illustrated by diagrams and photos. Each chapter is complete in itself, and the lucid style, coupled with the unequalled knowledge of the author, enables him to give his readers every opportunity of obtaining a thorough and clear grasp of each detail. Some of the most interesting chapters deal with the importance of liquid crystals in physics, chemistry, technics, and biology, and those on apparently living crystals and on the origin of life are deserving of special mention.

Das Ödem. ("Edema"). By Dr. MARTIN H. FISCHER. Translated into German by KARL SCHORR and WOLFG. OSTWALD. Dresden: Theodor Steinkopff. 1910. (M. 6).

IN this treatise the author gives the details of his thorough investigation of the phenomenon of oedema, discussing in all its aspects the hypothesis that it represents an increase above its normal value of the affinity of the colloids in the tissues for water. This increase may be said to be mainly due to an accumulation of acids in the tissues, owing either to an excessive formation of them or to their incomplete removal. The author's researches on the subject are of the first importance, and those chemists who are more particularly interested in the physiological side of the subject will find that they cannot afford to be ignorant of the descriptions of methods and results of investigations given in it. The work has been well translated into German, and Dr. Wo. Ostwald has contributed an interesting preface, in which he lays stress upon the importance of the problem of oedema both in general biology and pathology.

Untersuchung und Nachweis Organischer Farbstoffe auf Spectroskopischen Wege. ("Investigation and Detection of Organic Dyes Spectroscopically"). By JAROSLAV FORMANEK and Dr. EUGEN. GRANDMOUGIN. Part II. Section I. Berlin: Julius Springer. 1911. (M. 10).

THE arrangement of spectral apparatus for the investigation of organic dyes is discussed in this book, which also treats of spectroscopic methods of studying mixtures of dyes. The most suitable and satisfactory systems of classification of green and blue dyes into groups is explained, and the absorption and other properties of these dyes in water, ethyl alcohol, and amylate are tabulated. Reproductions of the absorption spectra are given in an appendix.

Messungen Elektromotorische Kräfte Galvanischer Ketten mit Wässerigen Elektrolyten. ("Measurements of the Electromotive Forces of Galvanic Batteries with Aqueous Electrolytes"). By R. AEBEGG, FR. AUERBACH, and R. LUTHER. Halle-a-S.: Wilhelm Krapp. 1911. (M. 8.40).

ALL the experimental material connected with the measurements of the electromotive forces of galvanic batteries with aqueous electrolytes is collected in a convenient form in this monograph, which is divided into three parts in order that reference to it may be as easy as possible. The first part consists of an index to the literature of the subject, arranged systematically and chronologically, and containing no actual figures but full references to the original papers. Part II. gives some results in tabular form, and the third part contains tables of the most probable values of the individual potentials. Only galvanic batteries in which pure aqueous electrolytes are used are taken into consideration, but every endeavour has been made to make the compilation complete as far as it goes.

CORRESPONDENCE.

PURIFYING MERCURY IN THE LABORATORY.

To the Editor of the Chemical News.

SIR,—Those of your readers who have charge of school laboratories especially will know that there is considerable difficulty in keeping a reasonably pure stock of mercury. Washleather, of course, will free it from dust and dirt, but, short of distilling, the methods given in ordinary text-books for purifying it are slow and not too satisfactory. There is a piece of apparatus figured in the dealers' catalogues under the name of Ostwald's Mercury Purifier, consisting of a funnel for holding mercury, a long wide tube to be partly filled with dilute nitric acid, and a capillary syphon tube at the bottom to deliver the purified metal. One is more or less out of touch with things here, so that I do not know if this contrivance is well known; if not, it deserves to be. As might be anticipated from the name attached to it, it is very effective; it will make 12 or 14 pounds of mercury pure enough for all ordinary purposes in a couple of hours, with practically no attention beyond occasionally re-filling the funnel; further, there is very little loss. My object in writing is to point out a simple improvement in the apparatus as usually sold. The funnel supplied has a piece of washleather at the end through which the mercury runs in a fine stream. My experience is that the washleather is destroyed in an hour or two by the nitric fumes, and thus the apparatus is rendered useless, for the essential point is to allow the metal to fall in the finest drops through the acid. I find, however, that by drawing out the glass tube of the funnel to a very fine point, the mercury will stream through this just as effectively as through the leather, and if it has previously been put through a piece of leather there is very little danger of the hole becoming clogged.—I am, &c.,

E. G. BRYANT.

Grey Institute, Port Elizabeth,
August 22, 1911

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 1, July 3, 1911.

Ketones of the Type of Benzylidimethylacetophenone.—A. Haller and Edouard Bauer.—By the action of *o*-, *m*-, and *p*-xylyl bromides on the sodium derivative of isopropylphenyl ketone the corresponding xylyldimethylacetophenones are obtained. They yield the xylyldimethylacetamides when treated with sodamide. The authors have prepared the xylyltrimethylacetic and *p*-methoxybenzylidimethylacetic acids and the corresponding alcohol, and have thus generalised the reactions which they have described in previous communications.

Chlorides of Iridium.—Marcel Delcpe.—The following compounds of iridium and chlorine have been described: IrCl_4 , $\text{IrCl}_3 \cdot 4\text{H}_2\text{O}$, IrCl_3 , and IrCl_4H . The author has prepared the first three of these, and has obtained results which point to the formation of readily soluble compounds which pass progressively to compounds which are less soluble. These phenomena result from successive condensations, which, however, cannot be expressed exactly in quantitative terms.

Uranic Dihydrate.—Oechsner de Coninck and M. Raynaud.—The authors have prepared uranic dihydrate, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, by two methods:—(1) By decomposing an aqueous solution of uranyl oxalate by means of light; (2) by treating uranous oxide with lukewarm hydrogen peroxide. They have reduced the dihydrate by pure hydrogen at a red-heat, and have thus determined the molecular weight of UO_2 . The mean of five experiments is 270.46.

Carbonates of Thorium.—Ed. Chauvenet.—The author has studied the action of carbon dioxide on thorium, and the action of an alkaline carbonate on a thorium salt. He finds that in the former case ortho carbonates are formed either neutral and hydrated, or basic and hydrated, or anhydrous. The neutral ortho carbonate has not been obtained. The action of heat transforms the neutral hydrated carbonates into the basic hydrated compounds $\text{CO}_4\text{Th} \cdot \text{ThO}_2 \cdot 1.5\text{H}_2\text{O}$ and $\text{CO}_4\text{Th} \cdot 3\text{ThO}_2 \cdot \text{H}_2\text{O}$.

Ketoglutaric Acids and Acid-Aldehydes of the Succinic Series.—E. E. Blaise.—If hydrobromic acid is added to oxalpyrotartaric ether a crystalline mass finally separates, and the etherification of the liquid residue gives three different fractions. That passing over at $143\text{--}145^\circ$ under 15 mm. consists essentially of the ether of the acid derived from methyl-ketoglutaric acid by the loss of one molecule of water. The fraction, which boils at $82\text{--}84^\circ$ under 11 mm., is the ethyl ether of pyrotartaric acid-aldehyde, and the other, boiling at $92\text{--}95^\circ$, is the corresponding ethoxylactone.

MISCELLANEOUS.

Battersea Polytechnic.—The Calendar of the Battersea Polytechnic for the new session, which opens on Monday, September 25th, gives full details of the numerous courses and classes held at the Institution. Full day and evening courses are in preparation for the Intermediate and Final Degree examinations in Science, Engineering, and Music. The lecturers in the various subjects are fully recognised by the University of London, so that students attending the Polytechnic may be registered as Internal Students of the University of London. In the Day Technical College full time courses are arranged in Mechanical, Civil, Electrical, and Motor Engineering, Architecture and Building, Chemical Engineering, and Art, the courses covering a period of three years, at the end

of which time students passing the necessary examinations are awarded the Polytechnic Diploma. Concurrently with the Diploma courses, students can prepare for and take the Degree courses in Science and Engineering of the University of London. The Training Department of Domestic Science offers two or three year courses in preparation for the teachers' diplomas in domestic subjects, and the Commerce Department gives a course extending over two or three years in preparation for Civil Service and other examinations, and for secretarial and other business appointments. Full and complete evening courses are provided in the Departments of Mechanical, Engineering, and Building Trades, Electrical Engineering, Mathematics, Physics, Chemistry, Natural Science, Photography, Art, Languages, Commerce, Women's subjects, and Music. Special mention may be made of the following new developments:—In the Mechanical Engineering Department a course of lectures on Illuminating Engineering. In the Electrical Engineering Department special attention is being given to the subject of Electrical Traction. In the Physics Department the course on Acoustics for Music students will be repeated, and a class in Physical Chemistry for chemistry students has been arranged. In the Chemistry Department the Chemical Engineering course has been extended by the addition of a practical class, and full courses are now provided in both the Minor and Major Pharmaceutical examinations. Attention may also be drawn to the Chemistry course for Sanitary Inspectors, and to the arrangements which have been made for the provision of special lectures by trade experts in connection with the Paper-making course. In the Natural Science Department the Botany classes now meet on four evenings per week, and courses covering four years are provided, also full courses in Advanced Hygiene, Human Physiology, Geology, and for Sanitary Inspectors. In the Commerce Department there are special classes in Economics, Accounting, History, and Geography. The Women's Department includes classes in Domestic Science, Dress-making, Needlework, Millinery, &c. It may be stated that the Edwin Tate Library has proved a great boon to students, the number of books borrowed by them having increased nearly 50 per cent during the session; many valuable additions have been made, so that there is now available for the use of students a really first rate library housed in a building of which the Polytechnic may justly be proud.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

German University Degrees.—Will any reader tell me the qualifications or Entrance Examinations a person must pass before entering a German university to study for a chemistry degree (Ph.D.). Also I should be glad of the addresses of one or two universities suitable for a chemist in an alkali works.—E. A. WHITE.

THE
DAVY-FARADAY RESEARCH LABORATORY
OF
THE ROYAL INSTITUTION.

Director:
Professor SIR JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday, for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

LENT TERM.—Monday, January 8, to Saturday, March 30.

EASTER TERM.—Monday, April 22, to Saturday, July 27.

Full Information and forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

THE CHEMICAL NEWS.

VOL. CIV., No. 2705.

THE INFLUENCE OF CONSTITUTION ON THE MOLECULAR VOLUMES OF ORGANIC COMPOUNDS AT THE BOILING-POINT.*

By GERVAISE LE BAS, B.Sc.

IF we consider the volume of 1 grm. atom of any one of the free elements and call it the atomic volume under the special conditions, we are dealing with a perfectly familiar physical quantity, and one which we believe stands for something which has a real and distinctive existence in nature. When an elementary atom enters into combination with others of similar or dissimilar nature, it does not lose its individuality, but appropriates a definite amount of space which is peculiar to itself and dependent (a) on its nature, (b) on the quantitative and qualitative character of its environment, and (c) on the physical conditions. This volume will in general be no longer the same as in the free element, nor indeed as in other combinations, because some or all of the above factors will be different.

Under certain circumstances—as at equal temperatures, the change in volume may be large, but if care be taken to make the comparison at corresponding conditions, then the difference $M.V. - \Sigma A.V.$ † will be a minimum, or may vanish altogether. Any residual differences under such circumstances may be ascribed to differences in constitution or even in complexity.

Our hypothesis then starts with the assumption that in the case of individual compounds, the molecular vol. = the sum of the volumes of the constituent atoms or $M.V. = \Sigma A.V.$, a statement which may sound as a truism, but is nevertheless important to remember, since it involves the conception of the distinctive character and integrity of the atomic domain.

The result is, that the law of additivity is true for compounds if they are considered individually, but the addition or subtraction of atoms or groups usually involve such changes, that it is only under very special conditions that the above principle is realised when comparisons are made between the volumes of different compounds. The reason is that not only is a particular volume impressed upon the entering atom or group to an extent partly dependent upon the nature of its environment, but also the atomic volumes of the other components of the molecular complex are also changed, and in general every atom has the size of its habitat adapted to the changed conditions. This is important, since the principle was never recognised in the older theories, nor is it universally admitted to-day. The principle also reveals the imperfect nature of the mode of investigation usually adopted and which is a legitimate one in the case of a strictly additive property, viz., the method of differences.

The method of investigation adopted is one which is based upon a principle which has been found to hold throughout the liquid state from the critical to the melting-point, and I imagine holds in the solid state also. The principle may be called the *law of constant atomic volume ratios*, and may thus be formally defined.

Law of Constant Atomic Volume Ratios.

In compounds of homogeneous structure the relations between the volumes of the atoms in each is the same under all physical conditions, and may be demonstrated at least approximately by a comparison of the volumes of similarly constituted compounds under comparable conditions, such as the boiling-point.

Secondly, if the compounds undergo changes in structure or are subject to particular constitutive influences, the usual changes in the actual atomic volumes do not, as a rule, involve changes in the relative atomic volumes.

The word "homogeneous" is intended to exclude such compounds of mixed structure as xylene, methyl cinnamate, &c., although the principle holds in these cases as well. The object is simply to preserve a distinction between an atom belonging to the nucleus and one of a similar kind belonging to a side chain.

The evidence upon which this law is based is in my opinion both ample and sufficient. The facts have already been published.

The first part of the above statement referring to the effect of physical changes on molecular volumes involves the idea of permanence of molecular form and configuration.

A similar idea of permanence of crystalline form is to be inferred from the constant relation existing between the equivalence parameters of Barlow and Pope under the influence of physical changes, and from the general nature of crystalline expansion.

An investigation of the volumes of a number of Sn-Sb alloys obtained by Vincentini and Omodei, both above and below the melting-point, has convinced me that the mode of expansion is similar in solids and liquids, and that the cause is to be found in the increased size of the atomic habitat under the influence of temperature. This is readily seen if it be remembered that in every case the molecular volumes of the solids are equal to the sum of atomic volumes of the free elements.

Prideaux's work on the volumes of the mercury-halogen compounds from the melting to the respective boiling-points is independent testimony to the truth of the law, for it can be shown that the volumes of Cl, Br, and I in the combined state at the boiling-point is similar to those of similar atoms in organic compounds. If now a constant relation exists between the molecular volumes under conditions of equal pressure down to the melting-point, it is because the individual atomic volumes diminish with changing physical condition in a similar ratio to the diminutions of the molecular volumes.

The above observations are important evidence in favour of the following conclusions:—

1. The structure of liquids is more nearly related to solids than to vapours.
2. The law of coincident states is intimately related to the law of additivity or a similar one, and departures from the latter involve changes in the former, the reasons being similar for both, viz., the influence of constitution.
3. It can be shown that the law of coincident states in liquids is not a consequence of Van der Waal's generalisations for vapours, being dependent on changes in atomic volume owing to changing physical condition.
4. However the volumes of compounds may change, the law of constant atomic volume ratios is always realised, whether the changes be physical or due to the influence of constitution.
5. Since it is not probable that the nature of liquid changes under various conditions of temperature, and that the above conclusions are true down to the melting-point, it is probable that the molecular interspaces are nearly, if not quite, negligible.

Various different views are now held as regards the constitution of liquids.

(a) Traube supposes that liquids are divided into two parts—one taken up by the molecules themselves, and

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

† In the expression $M.V. = \Sigma A.V.$, the term $M.V.$ refers to the volume of any substance at the boiling-point, $\Sigma A.V.$, or more precisely WS , where $S=370$ refers to the substance on the basis of a strictly additive theory. In a general sense $M.V. - \Sigma A.V. = 0$, or $M.V. = \Sigma A.V.$, but in this case $\Sigma A.V.$ refers to the actual atomic volumes of the substance.

equivalent to the quantity b of Van der Waal's theory, and the other the co-volume which is the space in which the molecules move. The latter is the same at a common temperature like 0° or 15° C. for all unassociated substances, and varies with temperature according to the well known gas law.

(b) Young and many others, while not subscribing to any particular system of molecular volumes, adhere to the idea that the conceptions of Van der Waal's are valid for the liquid state.

(c) Pridéaux considers that the co-volume under corresponding conditions in general, and the boiling-point in particular, is proportional to the molecular volume, although he does not concern himself with the particular magnitudes of the atomic volumes in the combined state. Comparisons are made between the observed volumes at the normal boiling-point, and also under other conditions of equal pressure. Similar comparisons are made between the observed molecular volumes and the sums of the volumes of the free elements under the various conditions.

(d) Kleeman considers that the sphere of action of the molecule is very nearly the same in magnitude as the distance of separation between the molecules in a liquid. It is further deduced that the factor expressing the variation of the diameter of the sphere of action with temperature must have the same value for all liquids at corresponding states.

(e) Richards, who introduces the conceptions of molecular and atomic affinity pressures, believes that the condition of things shown by Van der Waals to be true for vapours do not apply to liquids and solids; that the former approach more nearly to the latter in character than to vapours. It is also probable that in liquids the molecular interspaces nearly if not entirely vanish.

The views which are summarised in an earlier portion of this paper, and which have been advocated from time to time since 1907, approximate to those of Richards.

It is not necessary to refer to the now well-known conceptions of Barlow and Pope regarding the structure of crystalline solids, since we are here specially concerned with liquids.

It is now generally agreed that substances should be studied under corresponding conditions, which may be equal fractions of the critical pressures, the boiling-point or generally under conditions of equal pressure if the vapour pressures be small. The only point at issue is what proportion of the apparent molecular volume represents the sphere of influence of the molecule under the combined influence of the chemical and physical heat forces which act on the individual atoms.

Kleeman's view is easily made harmonious with that of Richards and that expressed in this paper, if we suppose that the radius of influence of the molecule is dependent on those of the individual atoms, and results from their motions of agitation for physical reasons. Moreover, if that constant factor which expresses the change in the volume of the molecule from one coincident condition to another be considered to result from similar changes in the atoms, we see that the law of constant atomic volume ratios is involved.

Pridéaux, who does not regard the matter from an atomic standpoint, at least from that of the combined atom, still adheres to the conception of a co-volume. It is, however, difficult to imagine a co-volume of the nature which he supposes to be due to molecular movements, for the co-volume is a function of the atomic nature of the molecule. In any case it is of the nature of a superfluity so far as molecular volumes are concerned.

The great objection to comparing the volumes at equal temperatures is that the affinity pressures of the atoms are not the same in different compounds under given conditions, and thus the volumes of similar atoms are different in each. For example, suppose that hexane, C_6H_{14} , at its boiling-point (71°) be changed to hexyl alcohol, $C_6H_{13}OH$, by the introduction of an O atom. As has been shown, this change in composition influences the volumes of all the

atoms in the molecule. It follows that at 71° neither the volumes nor affinity pressures will be comparable in the two compounds. For any comparison to be possible it will be necessary to raise the temperature to the boiling-point of $C_6H_{13}OH$, for then both the affinity pressures and the volumes will be similar.

There is another objection to Traube's method. Even if the results at 15° C. be accepted, they fail at other points. Thus, if the volumes of the normal paraffins from pentane to octane be plotted against temperatures starting from 0° and ending at the critical point, the curves will be found to cross; that for C_4H_{10} crossing successively those for C_6H_{14} , C_7H_{16} , C_8H_{18} , and so on. What, then, are we to understand by these points of intersection? If the two compounds which possess identical volumes at these points be considered to have similar co-volumes, must we conclude that the real molecular volumes of the two compounds are the same under the conditions? This is absurd and contradictory to what has been shown to exist at 15° C.

If the conclusions based upon the observations at common temperatures be true, then either the constitution of liquids must change between 0° and the critical point, or the law of coincident states is without significance.

The Variation in the Atomic Volume of H in a Typical Homologous Series at the Boiling-point.

The boiling-point is that at which molecular volumes may most conveniently be examined.

The significant atomic relations which have been pointed out are: $-C = 4H$, $O = 2H$ and $3H$, $N''' = 3H$, $Cl = 6H$, $Br = 7.6H$, $I = 10H$, $S = 6H$ and $7H$.

It is now possible to calculate the H equivalence W from a knowledge of the values for the constituent atoms, and if the molecular volume be V the ratio V/W gives the volume of H in the particular compound examined. If it were possible to do this for all the terms of a homologous series, say, up to C_{20} for instance, then it would be possible to find out how the volume of H, or for that matter of CH_2 , changes in a typical normal series with complexity.

The normal paraffin series has only been studied up to n octane, and thus the solution of the problem cannot be effected by a study of this series. If, however, we study the symmetrical monocarboxylic esters as determined by Gartenmeister, we find that the variation is exactly such as might be expected in a normal series. By calculating V/W for the various homologues up to octyl octylate, the characteristics of such a normal series is directly shown. The resulting curve presents some remarkable characteristics, which are common to many series. (See Table I., *prox.*)

1. The volumes of V/W or H for the initial members of a series are exceptionally large, but depend in magnitude on the complexity of these members.

2. The value then diminishes rapidly to a minimum at about the fifth term, about which the curve is nearly a horizontal straight line. It is under such conditions that the additive law is most nearly realised.

3. The value of H then increases gradually to about the seventh term, and then increases regularly in a linear way to the limit of the series.

4. The volume of H increases in value by 0.034 of a unit for every addition of CH_2 , as shown by calculation, and thus CH_2 shows an augmentation of about 0.204 for every addition of the homologous increment. Lossen assumed a different value in his well known formula.

If the first two members of each series be omitted, the volumes of the members may be numerically represented as follows:—

$$M.V. = WS + W(W-40)K \\ = W\{S + (W-40)K\}.$$

W represents the H equivalence of the compound, S the volume of H where the curve is nearly a horizontal straight line ($3.66-3.68$), and K , which is equal to 0.0055 or one-sixth of 0.034 , is a constant which expresses the increase in the volume of H occasioned by the addition of an atom H or its equivalent to a compound. The integer 40 indi-

cates the fact that the linear portion of the curve commences at complexity $W = 40$.

The results obtained for seven series show differences from the experimental values of only a few tenths per cent, which is practically the limit of experimental error. The formula thus consists of an additive portion, WS , and a term which is of a constitutive nature. The first depends on the complexity simply, and if we consider that the formula is a variation of the following—

$$M.V. = WS + W^2S,$$

the second depends on the square of the complexity. At any rate, the volume of H is expressed by the factor $S + (W-40)K$, and it is thus seen that its value depends on the nature of the molecule under given conditions. Mutual actions between the atoms in a molecule are consequently suggested, for the volume of the entering atom H or its equivalent will under given conditions be dependent on its surroundings, and there will be impressed on every other atom H or equivalent a corresponding volume. The result will be that the volume of H in no two compounds will be exactly the same, but will vary in a manner indicated by the above law.

It is remarkable that Lossen's well-known formula also possesses two similar terms, but the assumptions upon which it is based are defective, and the calculated numbers do not nearly so well represent the results.

The volumes of the atoms in normal series like that which has just been studied are the largest possible under the conditions. This is as it should be if the amount of independence is a maximum. Such a maximum of independence is realised by the straight chain arrangement of the C atoms or whatever closely related arrangement represents the truth. The point to notice is that C atoms in such an arrangement can only directly influence their immediate neighbours; but not those outside these limits. The other influence here contemplated is of a nature such as that which residual affinity might be supposed to exert on atoms not directly connected by means of valencies.

(To be continued).

OPTICALLY ACTIVE SUBSTANCES WHICH CONTAIN NO ASYMMETRIC ATOM IN THE MOLECULE.*

By Prof. WILLIAM HENRY PERKIN, F.R.S.,
and
Prof. WILLIAM JACKSON POPE, F.R.S.

WHILST pointing out the relation between molecular configuration and optical activity van't Hoff clearly indicated that substances which exhibit optical activity in solution do not necessarily contain an asymmetric atom in the molecule; whilst he pointed out that optical activity results from enantiomorphism of molecular configuration and showed that, in general, the latter type of enantiomorphism is recognisable by the presence of an asymmetric carbon atom in the graphic formula, he also made it quite clear that cases of optical activity might arise amongst compounds which contain no asymmetric carbon atom in the molecule.

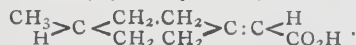
It is now known that a substance may exhibit optical activity in the amorphous or dissolved condition if its molecule contains an atom of quinquivalent nitrogen or phosphorus or of tetravalent sulphur, selenium, silicon, or tin. The most general case of optical activity distinguished by van't Hoff, that exhibited by a substance of enantiomorphous molecular configuration, but of which the molecule contains no asymmetric atom, has, however, not been realised until quite recently.

Van't Hoff referred to substances of the general constitution:—



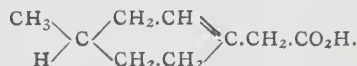
as being capable of existing in two enantiomorphously related molecular configurations. The symmetrical dimethylallene, $CHMe : C : CHMe$, which belongs to this class, should exist in two enantiomorphously related, and hence optically active, isomerides; although this substance has been prepared it is obvious that experimental difficulties will render difficult its resolution into optically active components.

As the most general case of optical activity is of profound theoretical importance, we have for a number of years devoted ourselves to its realisation. After a considerable amount of preliminary experimental work we decided that the most suitable compound belonging to this particular class is the 1-methylcyclohexylidene-4-acetic acid:—



The reason why this decision was arrived at is that whilst 1-methylcyclohexylidene-4-acetic acid contains no asymmetric atom in the molecule, but nevertheless possesses an enantiomorphous molecular configuration, it appeared possible to devise a method for its synthesis; and since it should be distinctly acidic in character it would be expected that its resolution could be effected by crystallisation with an optically active alkaloid.

We therefore devised a process for the synthesis of this acid (Perkin and Pope, *Trans. Chem. Soc.*, 1908, xciii., 1075). Curiously enough, however, whilst we were occupied with this work, Marckwald and Meth (*Ber.*, 1906, xxxix., 1171) indicated that they had also decided to prepare 1-methylcyclohexylidene-4-acetic acid and to resolve it into optically active components in order to realise the most general case of optical activity, and described the method by means of which they had synthesised and resolved the substance. The methods of synthesis adopted by Marckwald and Meth, on the one hand, and by ourselves on the other, were quite different and yielded quite different products; our acid melted at 66° , whilst that of Marckwald and Meth melted at $40-41^\circ$. We were, however, convinced that our method of synthesis yielded the compound of the constitution stated above, and that Marckwald and Meth's acid was the isomeric 1-methyl- Δ^3 -cyclohexene-4-acetic acid of the constitution:—



An acid of the above constitution obviously contains an asymmetric carbon atom and hence should be resolvable, as Marckwald and Meth found, into optically active components in the same way as large numbers of similarly constituted substances. We therefore disputed Marckwald and Meth's contention that their acid was 1-methylcyclohexylidene-4-acetic acid (*Proc. Chem. Soc.*, 1906, xxii., 107), and in reply these authors produced further evidence in support of their view (*Ber.*, 1906, xxxix., 2404); they had in this the support of Wallach, who was then of opinion that their acid had the constitution which they had assigned to it.

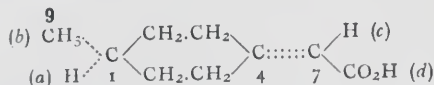
The difference of opinion briefly referred to above gave rise to a long controversy and led to an extended series of experimental investigations (Marckwald and Meth, *Ber.*, 1906, xxxix., 1171, 2035, 2404; Wallach, *Annalen*, 1907, ccxiii., 311; 1909, ccclxv., 255; Perkin and Pope, *Trans.*, 1908, xciii., 1075; Harding, Perkin, and Haworth, *Trans.*, 1908, xciii., 1943; Hope and Perkin, *Trans.*, 1909, xcv., 1360). The final result of this work was to prove conclusively that the original view taken by us was correct; the acid melting at 66° is the true 1-methylcyclohexylidene-4-acetic acid, whilst the acid melting at $40-41^\circ$, which Marckwald and Meth supposed to be the latter acid, is the

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

1-methyl- Δ^4 -cyclohexene-4-acetic acid, the graphic formula of which contains an asymmetric carbon atom.

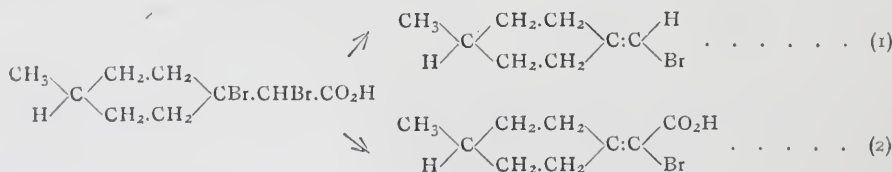
After our original view had been shown to be correct an improved method of preparing our acid was devised and its resolution effected by crystallisation with brucine (Perkin, Pope, and Wallach, *Trans.*, 1909, xcv., 1789). The *d*- and *l*-isomerids of 1-methyl-cyclohexylidene-4-acetic acid were ultimately obtained of the specific rotatory power $[\alpha]_D +$ or -81.1° ; each optically active component melted at 52.5° – 53° and the externally compensated mixture of the two at 66° .

The configuration of 1-methylcyclohexylidene-4-acetic acid may be represented in the following manner:—



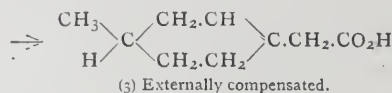
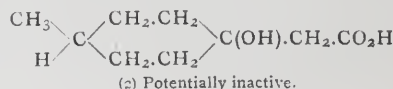
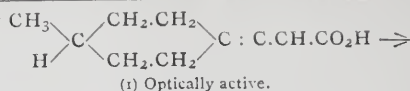
in which those bonds represented by unbroken lines all lie in one plane, and those represented by broken lines lie in a plane perpendicular to the first; if the continuous lines represent bonds which lie in the horizontal plane of the paper, the broken lines stand for bonds which lie in the vertical plane passing through the carbon atoms numbered 1, 4, and 7. It will now be seen that the plane of the paper which contains the continuous line bonds is not a plane of symmetry of the solid configuration, because the hydrogen atom marked (a), which lies outside that plane, is not repeated on the other side of the plane, the symmetrical position being occupied by the methyl group (b). Similarly the vertical plane remarked above is not a plane of symmetry of the configuration, because the groups (c) and (d), of different compositions, occupy symmetrical positions on the two sides of the plane. In the same way it can be shown that no other plane is a plane of symmetry of the configuration as above represented. Further, no directions can be distinguished as axes of symmetry of the solid configuration, nor can any point be located within it as a centre of symmetry. It is thus seen that when a highly symmetrical configuration is attributed to methane derivatives the configuration assignable to 1-methylcyclohexylidene-4-acetic acid possesses neither planes, axes, nor a centre of symmetry. The absence of all these elements of symmetry is more than is requisite to determine the enantiomorphism of the configuration.

In order to distinguish substances of enantiomorphous molecular configuration which contain no asymmetric atom in the molecule from those in which an asymmetric atom is present, it is convenient to describe the former as

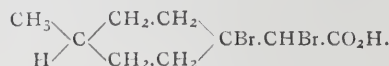


"centrosymmetric." The discovery of optically active centrosymmetric compounds opens up a wide field of stereochemical inquiry, part of which we have recently explored.

Thus, the centrosymmetric 1-methylcyclohexylidene-4-acetic acids can be converted into the 1-methyl- Δ^4 -cyclohexene-4-acetic acid of Marckwald and Meth, in which an asymmetric carbon atom is present; it became important to perform this conversion upon optically active material in order to ascertain whether optical inversion attends the change. On heating *l*-1-methylcyclohexylidene-4-acetic acid with water, sulphuric acid, and alcohol, the required conversion takes place, but the product, the acid of Marckwald and Meth, is optically inactive. It is concluded that the change occurs with formation of a saturated hydroxy-acid as an intermediate product, in accordance with the following scheme:—

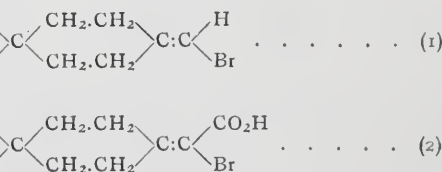


More importance attaches to the addition of bromine to the unsaturated centrosymmetric acid, a reaction which results in the formation of a saturated acid of the constitution—



The inspection of a stereochemical model of the molecular configuration of the unsaturated acid shows that the two atoms of bromine may be taken up in two distinct ways, each resulting in a configuration which contains an asymmetric carbon atom. The bromine atoms may become attached at the same side of the model as the methyl group or at the other side. In accordance with this prediction it is found that the externally compensated, *d*extro, and *l*ævo-1-methylcyclohexylidene-4-acetic acids each yield two dibromides, which may be distinguished as the α - and β -isomerides. Those obtained from the active acids are themselves optically active, and on mixing them in equal quantities the externally compensated dibromides obtained from the externally compensated acids are produced. No evidence of any optical inversion was obtained from the study of the bromination products.

The α - and β -dibromides just referred to undergo two simple reactions which reconvert them into compounds of the centrosymmetric type. On warming with sodium carbonate solution they lose carbon dioxide and hydrogen bromide, yielding 1-methyl-4-bromomethylenecyclohexane (1), and when heated with 50 per cent potash they lose hydrogen bromide alone, giving 1-methylcyclohexylidene-4-bromoacetic acid (2); thus:—



Both these reactions proceed quantitatively, and when carried out with the pure optically active α - or β -dibromides, yield pure optically active centrosymmetric products.

The bromo-hydrocarbon and the bromo-acid (1) and (2) readily combine with chlorine, yielding dichlorides which contain an asymmetric carbon atom in the molecule. When these compounds are prepared from optically active materials they are themselves optically active; each, of course, would be expected to consist of a mixture of two isomerides related as are the α - and β -dibromides.

It is very noteworthy that the long series of changes to which the centrosymmetric optically active 1-methylcyclohexylidene-4-acetic acids have now been subjected yield products which do, or do not, exhibit optical activity precisely in accordance with anticipations drawn from the study of the solid models representing the configurations

of the substances concerned. The conviction that the structural formulæ assigned to chemical substances imitate with considerable approximation to truth the real nature of molecular constitution was appreciably deepened by the introduction of the theory of the configuration of methane derivatives by van't Hoff and Le Bel; the development of the theory by Wislicenus, so as to embrace the configuration of ethylene derivatives, and by von Baeyer, in connection with polymethylene derivatives, has strengthened the view that the constitutional formulæ of organic chemistry represent very closely the actual atomic arrangement of molecular complexes. The considerations which led to the work described in the present paper involved, as has been seen, the development of the original simple conception of the space configuration of methyl and ethylene derivatives to an extent which may appear extreme. The fact that we have been able to show a close correspondence between the anticipations thus derived and the experimental results must be regarded as an independent demonstration of the fidelity with which constitutional formulæ depict molecular configuration.

THE INFLUENCE OF CARBON AND OTHER ELEMENTS ON THE CORROSION OF STEEL.*

(Concluded from p. 143).

Determination of Solution Pressures in Sea-water.

DETERMINATIONS of the solution pressures of the steels after prolonged immersion in sea-water have also been made with a view to ascertaining the influence of carbon on the electro-chemical positions of the various steels under conditions of galvanic corrosion. The results up to the present, however, are not sufficiently conclusive to warrant any definite statements in this direction being made in this report. The influence of the condition of the carbide upon the relative electro-chemical positions of the steels is, however, more definitely shown. In the case of a saturated steel it is found that after three weeks' immersion in sea-water the emulsified variety of pearlite is electro-positive to the diffused and laminated varieties, whilst the conversion of the pearlite into hardenite renders it electro-negative in this form to all the varieties of pearlite.

Determination of Solubility in Acid Solutions.

The solubilities of the various steels employed have been determined in 1 per cent solutions of H_2SO_4 and HCl , in order to determine the influence of carbon on the solubility of iron carbon alloys, and also to obtain an indication of the loss in weight per cent sustained on immersion in acid solutions, as contrasted with corrosion in such solutions as sea-water.

This was considered of importance in view of corrosion taking place under ordinary conditions, especially in large tanks, where atmospheric acids contained in the rain-water play an important part. This section is also of interest in the case of corrosion taking place in such solutions as acid pit waters.

The solubility tests were carried out on polished cylindrical bars of the steels ($1\frac{1}{2}$ inch long $\times$ $\frac{3}{8}$ inch dia.), which were separately immersed for a period of forty-eight hours in 100 cc. of the acid employed. The results obtained on immersion in 1 per cent H_2SO_4 are remarkably similar to those obtained in 1 per cent HCl , both as regards the actual values obtained with given specimens and in the type of influence exerted upon the solubility by the carbon per cent and the treatment. The two sets are consequently dealt with together, and the curves obtained with

1 per cent H_2SO_4 only are shown in Fig. 2. It may be noted that the practice of drawing smooth curves through the experimentally determined points has been adopted throughout in preference to the direct joining-up of these points by straight lines, as is sometimes carried out. The method adopted is found, in this case, to give much more satisfactory indications of the real positions of the critical points in the curve than the alternative one, whilst the possible degree of error introduced thereby is sufficiently small to be negligible.

The influence of carbon on the solubility is found to vary considerably according to the treatment previously undergone by the steel.

In the normalised rolled and annealed specimens the solubility rises very rapidly from 0.10 per cent up to 0.22 per cent, carbon approx., after which it falls abruptly, reaching a minimum at about 0.30 per cent to 0.40 per cent carbon. Further rise of carbon from 0.40 per cent to 0.96 per cent carbon produces a general, but somewhat irregular, rise in solubility in the normalised and rolled specimens, whilst in the annealed specimens a maximum solubility is reached at 0.60 per cent carbon, after which the values gradually decrease again to 0.96 per cent carbon. A comparison of these curves with those given by Heyn and Bauer (*Journ. Iron and Steel Inst.*, 1909, i., 109), as indicative of the probable influence of carbon percentage upon the solubility in 1 per cent H_2SO_4 , reveals very important differences. In the curves given by these experimenters no peak is observed at 0.22 per cent carbon owing to the absence of any steels between 0.14 per cent and 0.30 per cent carbon, and it is interesting to observe that in the absence of the intermediate steel (0.24 per cent carbon) in this series, the abrupt peak at 0.22 per cent carbon would have been entirely eliminated. In connection with this point it may be well to remark that careful microscopic examination fails to reveal any abnormalities in any of the micro-structures of the steels employed in this range of composition. A more important divergence, however, arises in the suggestion by these authors that the maximum solubility occurs at a "medium proportion of carbon"—presumably about 0.4 per cent to 0.5 per cent carbon. This is completely negated by these results, and in view of the fact that the steels employed by Heyn and Bauer in this range of carbon percentage also contain over 1 per cent Mn, it appears probable that this factor has exerted much more influence than was supposed by the authors themselves.

The tempered steels show a rapid rise in solubility with rise of carbon from 0.10 per cent to 0.30 per cent. This rise is followed by a range from 0.30 per cent to 0.55 per cent carbon, in which the solubility remains constant in the case of the specimens tempered at 500° C., and decreases in that of the specimens tempered at 400° C. After 0.55 per cent carbon a very rapid and regular rise in solubility occurs with rise of carbon to 0.96 per cent, the values given in the latter half of this range being higher than those given by steels of any other composition or treatment.

In the case of the hardened steels, the carbon tends to exert a similar type of influence to that described in the steels tempered at 400° C., this fact being more evident in the 1 per cent HCl results than in the 1 per cent H_2SO_4 results shown. The variations with carbon percentage, however, are very much less pronounced, and the total rise in solubility from 0.10 per cent to 0.96 per cent carbon is very small. In connection with the influence exerted by the condition of the carbide it is found that the conversion of the pearlite to hardenite considerably decreases its solubility (in both acids) as compared with all the varieties of pearlite. Little decisive difference is observed between the steels containing the laminated and diffused varieties of pearlite, whilst the resolution of the normal pearlite into the emulsified variety results in a decreased solubility below 0.2 per cent to 0.3 per cent carbon and a greatly increased solubility in the upper part of the range above 0.7 per cent carbon.

* Report of the Committee, consisting of Prof. J. O. Arnold (Chairman), Dr. W. E. S. Turner (Secretary), Prof. W. P. Wynne, Prof. A. McWilliam, Mr. C. Chappell, and Mr. F. Hodson. Read before the British Association (Section B), Portsmouth Meeting, 1911.

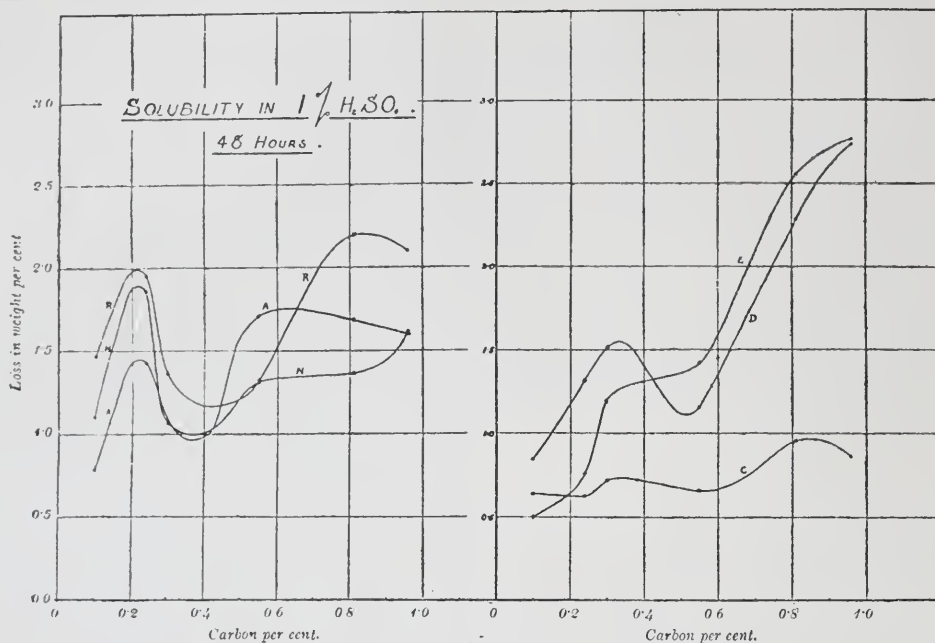


Fig. 2.

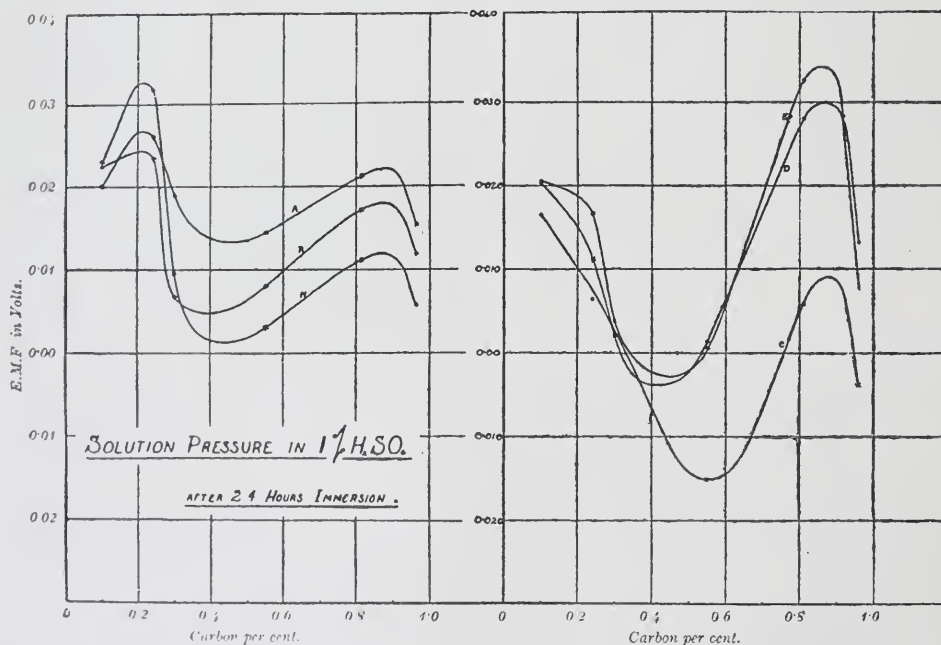


Fig. 3.

Determination of Solution Pressures in Acid Solutions.

The solution pressures in 1 per cent H_2SO_4 after twenty-four hours' immersion have also been determined, and these results (shown in Fig. 3) again indicate the influence exerted by the carbon to be of two main types.

In the annealed rolled and normalised steels—taking E.M.F. in volts and carbon percentage as co-ordinates—two distinct maxima are observed at 0.22 per cent carbon and saturation-point respectively, whilst the values for E.M.F. reach a minimum at 0.45 per cent carbon. The

values given at the 0.22 per cent carbon maximum are much higher than those at the saturation-point.

In the case of the hardened and tempered steels, the values of E.M.F. fall directly from 0.10 per cent carbon to a minimum at approximately 0.4 per cent to 0.5 per cent carbon, after which a rapid rise to a maximum at saturation-point takes place, followed by a sharp fall to 0.96 per cent carbon.

The relations between the values given by the various types of treatment are analogous to those noted in the

case of the solubilities. The hardened steels are consistently electro-negative to the other steels. The tempered steels are electro-negative to the annealed normalised and rolled steels below 0.50 per cent carbon, whilst the relative electro-chemical positions are reversed in the range from 0.7 per cent up to 0.95 per cent carbon. Very little difference is produced in this direction by difference in the tempering temperature, as is shown by the close agreement of the results given by the two tempered series. The divergence between the annealed normalised and rolled steels becomes quite distinct above 0.3 per cent carbon when the annealed steels become the most electro-positive, whilst the normalised steels take up the most electro-negative position in this group of steels when immersed in 1 per cent H_2SO_4 . Below 0.30 per cent C. the relative electro-chemical positions become confused and inconclusive. There appears little doubt that the results obtained in this section of the research indicate substantially the relative electro-chemical positions which would be taken up by the various steels on immersion under galvanic conditions in 1 per cent H_2SO_4 solution or in acid mineral waters of a similar type.

It will be observed that the resistance offered by carbon steels to disintegration when immersed in solutions varies considerably according as to whether the solution is of the sea-water type or is acid in character, and also as to whether the conditions of immersion are simple or galvanic in nature. It is impossible, therefore, to specify any particular composition or treatment offering the best resistance to attack under all conditions, and each case must be considered according to the circumstances involved.

ON THE PROPERTIES AND PREPARATION OF THE ELEMENT BORON.*

By E. WEINTRAUB.

I WILL describe the properties of the element boron isolated in pure fused form in the West Lynn Research Laboratory of the General Electric Company, and also give you in brief the methods used for the preparation of the element and a survey of its possible applications.

It will be best, perhaps, to first make you acquainted with the properties of the element (author shows a large lump of fused boron and small broken-up pieces, to show the fracture, and also a bottle filled with crushed boron).

Both in appearance and in its curved conchoidal fracture the lump and the broken-up pieces most nearly resemble black diamond. They are very hard, and scratch with ease the known hard substances except diamond. The surface is a very shiny black, and takes a beautiful polish.

To my knowledge this is the first artificial product (not an imitation of a natural product) which combines great hardness with an amorphous structure. Boron is, however, inferior to diamond of good quality in its strength. It rubs off rather readily on the diamond lap and even on the carborundum wheel. I do not consider it improbable that in further continuation of the work additional toughness may be imparted to boron, and the product become a cheap substitute for black diamond.

I have not determined the melting-point accurately, but estimate it to be between 2000° and 2500° C., nearer the second figure than the first.

Boron is a rather volatile element, its vapour tension being appreciable at 1200° C. It can, however, be fused readily not only under atmospheric pressure but also in vacuum.

The properties so far mentioned are in rather good accord with the position of the element in the periodic system. Boron has its place to the left of carbon, and has, so to say, right to be hard; conchoidal in its fracture—

both properties of fused carbon, and to have relatively high melting-point and a vapour tension of such magnitude that it volatilises to a considerable extent while melting in vacuum.

In fact, this similarity of properties might be used to determine in its turn properties of carbon. Thus the high vapour tension of boron would make it probable that the volatilisation of carbon at high temperatures (as in incandescent lamps) is a thermal process, and not due primarily to electric discharges or chemical processes. The search for a form of carbon having a low vapour tension comparable with that of metals such as tungsten would, in the light of this, be futile, and I admit that the argument is weighty enough with me to have caused me to singularly reduce my efforts in that direction.

We come now to a property of boron which is entirely unexpected, and places boron in a position all by itself. I refer to its electrical characteristics. When cold, boron is a very poor conductor, its specific resistance being about 10^{12} times that of copper. In this it still shows its similarity to amorphous carbon, which is a very poor conductor, and to diamond, which is an insulator. But where it differs is in the abnormal value of its temperature coefficient of resistance. The resistance of boron very rapidly drops as the temperature rises, so that between room temperature and dull red heat (400°) the resistance drops in the approximate ratio of 2×10^6 to 1. Around room temperature the resistance falls to half its value for every 16° C. In other words, the resistance drops geometrically with arithmetic increase of temperature. The law is, however, only approximate. If extended over large temperature intervals, the interval corresponding to equal resistance ratios increases with the temperature. The relation between temperature and resistance was studied quantitatively up to red heat. When red heat is reached the resistance, however, still continues to drop rapidly.

This enormous influence of temperature on the resistance of boron, combined with the fact that it occurs at ordinary temperatures, makes the behaviour of boron as an electrical conductor entirely different from that of ordinary conductors. Thus Ohm's law becomes useless almost to the same extent as in case of gaseous media. In fact, the behaviour of boron is more like that of a spark gap or arc than that of a solid conductor. There exists, for instance, a "break-down" voltage in case of boron as in that of an air gap. Below the break-down voltage only very small current flows through a boron conductor, but once current is started (the air gap is "bridged" over) boron becomes a relatively good conductor.

The potential drop across a boron conductor falls first very rapidly as the current increases, but has a tendency to become constant, and is usually approximately constant through quite a range of current. This potential current curve is again very much like that of a discharge through gases.

The conception of a steadying resistance which has the function of preventing the conducting medium from running away is applicable as in the case of arcs.

Similarly to arcs it is impossible without special arrangements to run two or more boron conductors in parallel as one robs the others of current.

Before an audience of chemists, these remarks on the electrical characteristics of boron will suffice. To the electrician there is almost an endless variety of surprising phenomena.

Speculation as to the cause of this abnormal behaviour of boron might be of interest, but I would like to emphasise only the following point, namely, that the enormous drop in resistance here takes place in an elementary substance, the conductivity of which is wholly metallic. Whatever theory may be proposed for the explanation of the behaviour of boron, this fact must be taken as fundamental.

In fact, the abnormal value of the temperature coefficient (as well as the high specific resistance) are peculiar properties of pure boron. When foreign elements are added

* Address presented before the North-Eastern Section of the American Chemical Society, February 17, 1911. From the *Journal of Industrial and Engineering Chemistry*, May, 1911, iii., No. 5.

to boron the conductivity increases (in analogy to ordinary solutions), and the temperature coefficient of resistance becomes reduced in value until with a sufficiently large percentage of the foreign element the characteristic properties are entirely obliterated.

Boron presents a very grateful case for exact measurements, as the drop in resistance occurs at ordinary temperatures, and it would be very desirable to determine the temperature resistance curve with great accuracy. The curve thus obtained would be of theoretical interest, and could also be used as the basis of a very delicate method of temperature measurements.

It would also be interesting to determine the law connecting the resistance of boron and its negative coefficient of resistance with the amount of foreign elements, such as carbon, magnesium, &c., added. The effect of these additions is very large, and I have determined it with only an accuracy sufficient for technical purposes, but it would be interesting to find out the exact relation between the concentration of the dissolved substances and the conductivity as well as the coefficient of resistance. I am inclined to believe from my experiments that the law is an exponential one.

And now that I am started in the direction of suggesting work for others, I am tempted to make a few more suggestions as to lines of work which I for the immediate present cannot take up.

It would be interesting to measure the heat conductivity of boron at different temperatures, and compare it with the electrical conductivity. If the parallelism between these two which holds in the case of metals should hold approximately in the case of boron, then we should expect an enormous increase of the heat conductivity with the temperature.

It would also be interesting to study the specific heat of boron at different temperatures. Weber had at his disposal only impure boron powder, and his results must therefore be unreliable.

No matter how interesting the investigations outlined would be, there are others of technical nature referring to applications of boron to electrical machinery, telegraphy, &c., which at present require all my attention, and I am in the position of a man who is regretting that he cannot find more than twenty-four hours in a day.

I will now give a brief description of the methods used in the preparation of the element.

We are using two different methods. In the first we start with the reduction of boric anhydride by magnesium. This reaction was carried out by various chemists, beginning with Berzelius, Wohler, &c., and recently by Moissan. I must refer for a description of the results obtained by myself to my article in the *Transactions of the American Electrochemical Society*, 1909, vol. xvi. It will suffice here to state that as a result of a thorough study of the reaction we made one step in advance of the previous workers—we found, that under certain conditions of temperature, proportion of reacting substances, &c., a perfectly homogeneous product is obtained which contains as chemical constituents only boron and oxygen, in proportions very nearly corresponding to the formula B_2O . We called the substance "boron suboxide" without, however, desiring thereby to express a definite opinion as to its chemical nature. At the time this seemed to be an important improvement, as the elimination of magnesium from the final product seemed to be desirable. Further work has shown, however, that in the treatment to which the impure product has to be subjected in order to obtain pure boron it matters little whether the impurity is oxygen or magnesium or nitrogen, &c. (The preparation of boron suboxide free from other impurities proved, however, useful in connection with the solution of the problem of producing sound copper castings for the description of which the reader may be referred to the *Transactions of the American Electrochemical Society*, 1910, vol. xviii.). This treatment consists in heating the impure boron whether containing boron suboxide or magnesium boride or nitride to a temperature

near the melting-point of boron. At this temperature all these compounds dissociate, magnesium and nitrogen come off as such, oxygen as boric anhydride.

The main difficulty encountered in the development of this method was that of obtaining on a large scale high temperatures in the neighbourhood of 2000° without the use of carbon in any form whatever, as boron has a great affinity for carbon and carbonaceous gases at that temperature.

The second method is based on the decomposition of boron chloride by hydrogen at good red heat. This reaction is carried out in two different ways:—(1) In an arc discharge taking place between two boron or water-cooled copper electrodes in an atmosphere of boron chloride and hydrogen, and (2) by deposition on a hot graphite tube heated by current passing through it. The temperature and conditions can be so adjusted that practically no combination takes place between the boron and the graphite, and very pure boron can be obtained. Boron chloride is best prepared by passing chlorine over boron carbide, which latter can be made in the electric furnace from boric anhydride and carbon.

I want to add a few words on the possible applications of boron in science and industry.

The first thing that suggests itself is its use for accurate measurement of temperatures. In view of the exceeding accuracy of electrical measurements and the rapid change of resistance of boron with the temperature, an accuracy in temperature measurements could be obtained which would be greater than anything yet available, especially as the boron resistor could be introduced in form of a very small filament, thus disturbing but very little the thermal conditions. Of course, the boron thermometer would have to be calibrated, and above red heat it would have to be enclosed in an envelope filled with inert gas.

Closely connected with this would be the use of boron as a temperature regulator in a way so obvious as to require no particular description.

Finally, in the same line of thought, boron could be used for measuring radiant energy. A rough surface of boron would probably behave very nearly like a black body, but if necessary a part or the whole of its surface could be covered with fine carbon. One way in which the measurement of radiant energy could be carried out would be by determining the radiant energy input as a difference between electrical energy inputs before and after the radiant energy falls on the boron piece. The temperature of the boron piece is recognised to be the same by the fact that its resistance is the same. This ought to be a very delicate zero method.

The industrial applications, however, are those which have first claim on my attention. Without going into details, I may say that these are based on the electrical characteristics of boron and on its mechanical properties.

The last drop of resistance with the temperature which transforms boron under certain conditions from a very poor conductor for normal voltages into a good conductor for abnormally high voltages is certain to make it valuable for protection of electrical circuits.

The potential current curve which shows a drop in potential with increase in current makes possible the use of boron either alone or in connection with an ordinary resistance (so as to give a unit with a constant potential drop) for the purpose of regulating electrical machinery.

The influence of small amounts of other elements (carbon especially) on the specific resistance and temperature coefficient of boron, which was described above, gives a very delicate means for adjusting the boron resistor to any prescribed requirements.

The valuable mechanical property of boron consists, of course, in the fact that it combines hardness with amorphous structure, and in the course of our work we have already succeeded in producing meter jewels superior in quality to sapphire.

Will it be possible to approach the properties of diamond or perhaps by combining boron and carbon even exceed

diamond in its hardness? I can only say that we are working on this problem.

In conclusion, I wish to attract your attention to the close interrelation of electrical and chemical methods in the work I have tried briefly to describe to you to-night. The investigation was started originally for the purpose of determining whether boron is a suitable element for incandescent lamp filaments. In the course of the investigation, in order to isolate the element, electrical methods had to be used to obtain the high temperatures needed. In fact, the isolation of the pure element is practically impossible without the use of electrical methods, and the failure of previous chemists can easily be explained by the fact that they did not possess the necessary electrical tools. Finally, after the chemical problem had been solved and the element isolated its main applications have been found again in electrical machinery.

How many other interesting and useful applications may not yet be found in this vast field of electro-chemistry in its broadest sense?

A STUDY ON THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.*

THE CHIEF SOURCES OF ERROR IN THE METHOD.

By E. M. CHAMOT, D. S. PRATT, and H. W. REDFIELD

(Continued from p. 148).

V. Errors Due to Variations in the Alkali Employed.

It has long been recognised that the same alkali must be added to the water residue being tested as that with which the standard has been prepared. But there do not appear in the literature any data showing just what the difference in colour intensities may be when using different alkalis, nor which alkali gives the darkest colour and therefore permits of the recognition of the smallest amount of nitric nitrogen.

In the method as originally described, ammonium hydroxide was employed to render the liquid alkaline and develop the yellow colour. Ammonia fumes are decidedly objectionable in a laboratory devoted to water analyses where determinations of free and albumenoid ammonia must be made. Where such conditions obtain a fixed alkali must be substituted in accordance with the suggestion of Hazen and Clark (*Journ. Anal. Appl. Chem.*, 1891, v., 301), but these investigators give no data upon which to base a decision as to the alkali to be preferred. It was also important that experiments be performed in order to learn the influence, if any, that an excess of alkali might have on the colour.

It had already been ascertained that potassium hydroxide gave yellow colours as intense or slightly more so than the other alkalis (Chamot and Pratt, *loc. cit.*), hence the employment of the tripotassium salt of the nitrophenolsulphonic acid as standard.

Experiments were made to ascertain the effect of variable excess of alkali. The following table shows the average results obtained by using varying volumes of 12 normal alkali in excess. In these runs the residues contained 6 parts and 10 parts per million of nitrogen as nitrate respectively.

Comparisons were made with the permanent tripotassium salt standards.

Parts per Million Nitrogen Indicated.

Cubic centimetres 12 N alkali in excess.	With KOH.		With NaOH.		With NH ₄ OH.	
	6 parts.	10 parts.	6 parts.	10 parts.	6 parts.	10 parts.
Just alkaline..	6	10.2	5.2	9.2	4.1	7.5
2 cc.	6	10	5.2	8.9	4.8	8.5
5 cc.	6	10	5.3	9.0	4.9	8.8
10 cc.	6	10	5.6	9.2	4.9	9.5
Over 10 cc. . .	—	10	—	9.2	—	9.5

Other trials with different nitrate content were made with relatively similar results. It appears, therefore, that potassium hydroxide yields darker colours, and that a decided excess of alkali does not appreciably affect the results. In the case of potassium hydroxide, however, it is essential that there be always an excess, since the colour just at the neutralisation point is slightly reddish and therefore appears darker than when there is a drop or two in excess. For reasons not ascertained ammonium hydroxide has yielded variable results, but since this alkali was otherwise undesirable no further investigations were made.

VI. Error Due to the Presence of Organic Matter in Water.

The residue from a water containing organic matter, when acted upon by the strong sulphuric acid of the reagent, gives rise to brown colours, either before or after the alkali is added, that often completely mask any yellow due to nitrates. This source of error has been so long known and so well recognised that comparatively little time was spent in its study. Many methods have been suggested for removing the organic matter, such as potassium permanganate in acid solution, or in alkaline solution, basic lead acetate, animal charcoal, aluminium cream, &c. Of these methods aluminium cream has proved the most satisfactory and practicable in our hands when dealing with the usual type of waters used for household and municipal purposes in our section of the United States. In all but very exceptional waters the removal of the colouring matter by this process has been found sufficiently complete and no losses of nitrates have been observed.

VII. Errors Due to Mechanical Losses on Evaporation or during the Addition of the Acid Reagents.

Leeds (*Am. Journ. Sci.*, 1874, [3], vii., 197) has stated that nitrates are slightly volatile at 100°, and Fox (*Tech. Quart.*, 1887, i., 54) has found nitrates in the distillate from a solution of potassium nitrate. Gill (*loc. cit.*) found a slight difference in his results ascribed to loss on evaporation, but so small as to be considered within the limits of error of the method.

Until the tripotassium salt standard was adopted in the present investigation it was found practically impossible to properly interpret the results obtained, but with an available standard at hand it was found that the losses on evaporation were negligible, and that the slight variations in colorimeter readings of three different observers were as great as any indicated differences which might be ascribed to evaporation losses.

The method employed in this study consisted in evaporating on the water-bath equal volumes of water containing known amounts of nitrogen as nitrate. These residues were treated with standard reagent as usual, after various periods of continued heating of the dry residue, and finally were compared with tripotassium nitrophenoldisulphonate standard.

The following are some of the results obtained with 1, 2, and 10 parts per million of nitrogen as nitrate.

Time of heating after residue became dry.	Parts per million of nitrogen found.		
	1.0	2.0	10.0
30 min.	1.1	1.9	10.0
1 hour	1.0	1.9	10.1
2 hours	1.0	2.0	10.0
4 hours	1.0	2.0	10.2
7 hours	—	—	10.0

The slight differences in the readings are undoubtedly due to the presence of the mono-para acid in the reagent, for runs made with a disulphonic acid reagent free from mono acids gave even better results. Other runs with different quantities of nitrogen were made with similar results. It appeared, therefore, that any losses arising from heating the dry residue in a water-bath are not measurable in colorimeters of the types commonly employed. However, it seemed wise to carry the study

* From the *Journal of the American Chemical Society*, xxiii., No. 3.

a trifle further. After a sample had reached dryness, distilled water free from nitrates was added and evaporated to dryness. This process was continued many times. Finally the residue was treated with the reagent, diluted, and made alkaline. No measurable loss of nitrogen could be detected.

The fact that the final colours obtained matched those of the permanent tripotassium salt shows that the thin film of reagent covering the residue is sufficient to hold the nitric acid set free by the strong sulphuric acid of the reagent, and that any losses due to incomplete nitrification are not measurable. Nevertheless, to make assurance doubly sure, samples of water were evaporated in deep crucibles, adding a little at a time so as to have the residue substantially all on the bottom. A rapid application of reagent then gave a much greater thickness of sulphonic acid over the residue. Identical results were thus obtained; in no case was the final colour appreciably darker as measured in long Nessler tubes or in a Wolff colorimeter.

The addition of the reagent causes losses in particular cases, however, as, for example, when carbonates or chlorides are present.

VIII. Errors Due to the Presence of Carbonates in the Water Residue.

The addition of the sulphonic acid reagent to residues containing much carbonate causes more or less violent effervescence, due to the liberation of carbon dioxide and a consequent mechanical loss of nitrate, causing, in some cases, considerable error. This was proved by evaporating waters in round-bottomed flasks, which were then closed with a two-holed stopper carrying a separatory funnel and bent glass tube leading into nitrate-free distilled water. The reagent was added to the residues through the funnel and the evolved gases swept over into the distilled water by nitrate-free air; this water was then made slightly alkaline and evaporated to dryness. The residue treated in the usual manner showed the presence of nitrates, while blank tests made on carbonates showed none. No uniform loss was found among many samples of water having similar nitrate and carbonate contents. This was to be expected, as the exact rate of adding the reagent, and the method and the rapidity of its distribution over the residue, would naturally materially affect this loss. This loss, however, is insignificant save when the alkalinity of the water is very high or the amount of nitrate present is very low; when these conditions obtain the loss may be easily prevented by adding to the sample before evaporation an amount of 0.02 N sulphuric acid sufficient to nearly but not quite neutralise the alkalinity.

At this stage of the investigation word reached us from Prof. Bartow, of the University of Illinois, that he believed that Robert Spurr Weston was at work upon errors due to carbonates. Correspondence with Mr. Weston brought out the fact that he and his assistant, Miss Helen R. Hosmer, had already made sufficient progress on the investigation to demonstrate that carbonates do introduce very appreciable error in the sulphonic acid method.

Weston and Hosmer very kindly placed the results of their investigations in our hand, and it is with great appreciation of their courtesy and kindly interest in our study of the sulphonic acid method that the following results are quoted from their unpublished notes.

"The work was done in March, 1909. We were at a loss to explain the freakishness of the results we were getting with some highly nitrated sewage effluents, and thinking that possibly it might be due to the presence of carbonates, we made a rough experiment as follows:—

"Six samples of distilled water, each containing 0.006 mgrm. of nitrogen in the form of potassium nitrate, were evaporated to dryness, three of them with the equivalent of 2, and three with the equivalent of 5 mgrms. of calcium carbonate. When treated with phenolsulphonic acid and compared in the ordinary way the approximate readings were as follows:—

Mgrm. nitrogen taken.	Mgrms. calcium carbonate, equivalent to sodium carbonate added.	Mgrm. nitrogen determined.
0.006	2.0	0.004
0.006	2.0	0.004
0.006	2.0	0.005
0.006	5.0	0.002
0.006	5.0	0.002
0.006	5.0	0.002

"This experiment shows plainly that the presence of carbonates interfered with the formation of colour. In order to approximate more nearly the conditions found in natural waters the experiment was repeated with smaller quantities, as shown in the following table:—

Mgrm. nitrogen taken.	Mgrm. of calcium carbonate added.	Mgrm. nitrogen determined.		
		A.	B.	C.
0.005	0.00	0.004	0.004	0
0.005	0.05	0.004	0.004	—
0.005	0.1	0.003	0.004	—
0.005	0.25	0.003	0.003	0.004
0.005	0.5	0.002	0.002	0.003
0.01	0.05	0.008	0.008	—
0.01	0.1	0.007	0.007	—
0.01	0.25	0.006	0.006	0.006
0.01	0.5	0.005	0.005	0.005
0.01	0.00	0.010	0.010	—

"It was evident from this experiment that the carbonate prevented the formation of the yellow colour to some extent. To confirm our impressions that this was due to the presence of carbon dioxide, evolved when the acid was added to the residue, and not to the presence of the base (potassium, sodium, calcium, &c.), we evaporated samples containing 0.01 mgrm. of nitrogen in the form of potassium nitrate to dryness, treated them with phenolsulphonic acid, and after diluting them with water, passed carbon dioxide into three of the samples for about five, ten, and twenty-five minutes respectively. The results were as follows:—

Mgrm. nitrogen taken.	Minutes exposure to CO ₂ .	Mgrm. nitrogen determined.
0.01	5	0.008
0.01	10	0.006
0.01	25	0.005

"These experiments proved that the introduction of the gas destroys the colour-producing compound.

"Experiments were made to show whether or not the presence of atmospheric carbon dioxide had any effect upon the determination, and for this purpose several samples were evaporated in an atmosphere of dioxide without affecting the determination of the nitrogen. Free carbon dioxide has no effect as it is expelled during evaporation, that is, before the phenolsulphonic acid is added.

"The above were only preliminary experiments and are mainly of suggestive value. They were not continued after we heard that you were studying the determination.

"Our suggestion for the overcoming of this difficulty is to add acetic acid to the water before evaporation. No experiments were made along these lines, however, beyond evaporating some of the standard with such amounts of sodium acetate as would be formed were acetic acid so added. This did not prevent the determining of the full amount of nitrogen present.

"Whether or not an excess of acetic acid added to ordinary waters would cause volatilisation of nitrogen from the acid solution during the evaporation of the samples we cannot say. We feel sure from our experiments that if the alkalinity of the water be not destroyed by so doing that it may be used with good results."

In view of the above quoted results, it did not appear necessary to spend further time upon the study of the effect of carbonates on the standard reagent, and all further work was confined to reagents containing no mono-

sulphonic acids. In the latter case the same small mechanical losses were again observed. No appreciable change in final colour could be observed even after twelve hours' passing of carbon dioxide through the treated residue before the addition of the alkali.

(To be continued).

NOTICES OF BOOKS.

Cold Storage, Heating, and Ventilation on Board Ship.
By SYDNEY F. WALKER, R.N., N.I.E.E., M.I.M.E.,
N.C.S.I.A., M.Inst.M.E., London; Constable and
Co., Ltd. 1911. (8s. net).

IN this book cold storage is treated mainly from the point of view of the naval or marine engineer, and different forms of refrigerating apparatus which can be installed upon board ship are described with illustrations. A comparatively large amount of space is given to the discussion of faults, and the best way to track them down to their origin and correct them is carefully explained. In fact, the author has thoroughly realised that one of the chief uses of a book of this kind is to help the engineer in the event of a breakdown, and to enable him to foresee and avoid minor accidents and troubles. The second part of the book deals with the heating and ventilation of ships, and the best methods employed on both sides of the Atlantic are fully discussed, both as regards their principle and their practice.

The Relative Volumes of the Atoms of Carbon, Hydrogen, and Oxygen when in Combination. By HAWKSWORTH COLLINS. London: Morton and Burt, Ltd. 1911.

IN this book the author gives the data upon which he has based his values of the relative volumes of the atoms of carbon, hydrogen, and oxygen. He ascribes to carbon one of two definite volumes which it occupies in accordance with certain fixed rules. Thus its usual volume is 0.71, but when it is united with the two valencies of an atom of oxygen it becomes 8.0. Similarly, oxygen has three possible volumes and hydrogen four. Thus the existence of nine different constants is assumed. Hence the molecular volume of 100 organic compounds has been calculated, and by dividing the molecular weight by the molecular volume a calculated value of the specific gravity is obtained. When this calculated value is compared with that determined experimentally a remarkably good agreement is observed, and it is hardly conceivable that it could be due to coincidence. In spite of a certain amount of artificiality in the author's conceptions, as when he speaks of "that part of an element from which one valency emanates," it is only fair to say that his work merits the careful attention of physical chemists. The method of calculation seems rather less empirical than that based upon Kopp's formula.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 11, 1911.

Distillation of Tin in Vacuo.—Erich Tiede and Franz Fischer.—Although tin has a low melting-point (230°) its boiling-point is very high, and hence it is difficult to distil it. The authors have constructed an apparatus in which it is possible to obtain high temperatures in a vacuum, and have thus succeeded in distilling

tin. They have investigated the properties and reactions of the products obtained by the distillation of various commercial varieties of tin, and have obtained the pure metal free from sulphur.

Syntheses with Yellow Phosphorus.—J. Mai.—Hot solutions of sulphur in aromatic hydrocarbons readily take up yellow phosphorus, and at high temperatures the products crystallise. P_4S_7 and P_4S_{10} can thus be prepared, naphthalene being used as the solvent. The author has also obtained phosphorus sesquiselenide, P_4Se_3 , and hopes to prepare higher selenides from it.

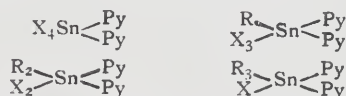
Action of Hydrofluoric Acid on Zirconium Oxide.—E. Wedekind.—When aqueous hydrofluoric acid acts on zirconium oxide the tetrafluoride is formed, but on evaporation it is partially hydrolysed. When ignited the tetrafluoride volatilises and the residue is oxide, which can also be volatilised as tetrafluoride by repeating the operation. In presence of a sufficient quantity of sulphuric acid the tetrafluoride is converted into sulphate or zirconium sulphuric acid, which gives the oxide on ignition.

Tellurium Carbide, CTe_2 .—A. Stock and Herbert Blumenthal.—Tellurium was volatilised in the arc under thoroughly cooled carbon disulphide, the anode being Acheson graphite. When all the tellurium had volatilised the yellow solution was filtered and concentrated, and then distilled in a current of CS_2 . The distillate contained a very small quantity of a volatile compound of carbon and tellurium. Analysis showed that it was the ditelluride, CTe_2 , corresponding to carbon disulphide. It is exceedingly unstable and possesses an unbearable smell. It is very soluble in CS_2 and in other organic solvents.

Preparation of Colloidal Silicic Acid.—E. Ebler and M. Fellner.—Perfectly clear and stable silicic acid-sol can be prepared by passing silicon tetrachloride vapour, mixed with a dry indifferent gas, into water, and thoroughly stirring. Ten to 20 grms. $SiCl_4$ must be used to every 500 cc. of water.

Zeitschrift für Anorganische Chemie.
Vol. lxxi., No. 2, 1911.

Pyridine Compounds of Tin Haloids.—P. Pfeiffer.—Four series of double salts of tin haloids and pyridine exist:—



These correspond in constitution and composition to the alkylated and phenylated double tin salts. The co-ordination number of tin is again proved to be six. Both $SnCl_4Py_2$ and $SnBr_4Py_2$ are white amorphous infusible powders which are very stable. Monomethyl tin chloride and monomethyl tin bromide are also white amorphous powders, obtained from their constituents. The dimethyl tin haloids also combine with 2 molecules of pyridine, as well as the diethyl, dipropyl, and dibutyl compounds, giving derivatives such as $(C_2H_5)_2SnCl_2Py_2$. The diphenyl tin haloids form well defined compounds with more than two pyridine molecules.

Rôle of Iron as Catalyser in Synthesis of Ammonia under Pressure.—Karl Jellinek.—In this paper the author describes an apparatus which can be used for the investigation of gas reactions at high pressures and high temperatures, and in which the space in which the reaction takes place is completely cut off from the exterior. At 870° iron can dissolve or adsorb considerable amounts of ammonia. If the dissolved or adsorbed product of synthesis does not leave the catalyser too slowly, it is possible for the equilibrium to be greatly exceeded in the reaction chamber.

Labradorite-norite with Porphyrific Labradorite Crystals.—J. H. L. Vogt.—The author has investigated the process of crystallisation of the eruptive rock

labradorite in order to see whether it can be explained on the basis of the laws of physical chemistry, and has thus confirmed his earlier work.

Zinc Peroxide (Zinc Monoxide, Zinc Peroxydate), $\text{ZnO} \cdot \frac{1}{2} \text{H}_2\text{O}$.—E. Ebler and R. L. Krause.—To prepare zinc peroxide an ethereal solution of 1 molecule of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ is made, and to it is added in small quantities $1\frac{1}{4}$ molecules of H_2O_2 . The white amorphous precipitate is washed with dry ether. It behaves like a true peroxide of zinc; it gives up oxygen with dilute acids and when heated, ZnO remaining in the latter case. It slowly undergoes hydrolysis with cold water.

Ammonium Carnallite.—Wilhelm Biltz and E. Marcus.—Ammonium carnallite crystallises from a solution of equivalent amounts of NH_4Cl and MgCl_2 at temperatures above 40° . With ordinary carnallite it forms three kinds of mixed crystals:—(i.) Those of the type of ordinary carnallite, containing up to 15 molecules per cent NH_4 . (ii.) Those of the type of ammonium carnallite, containing 27 to 100 molecules per cent NH_4 . (iii.) Monoclinic crystals, containing between 15 and 27 molecules per cent NH_4 .

Aluminium Sulphide.—Wilhelm Biltz and Fritz Caspari.—When a powdered mixture of metallic aluminium and sulphur is covered with fused sulphur in a crucible and ignited by means of a magnesium ribbon, a violent reaction occurs and a crystalline mass is left in the crucible. This raw product may be purified by sublimation. Al_2S_3 crystallises hexagonally. Its specific gravity is 2.02 , and its melting-point is $1100 \pm 10^\circ$. The authors have confirmed the existence of Regelsberger's monosulphide of aluminium.

Formation of Oxidising Agents in Atmospheric Air by Ultra-violet Rays.—Witalius Chlopin.—In ordinary atmospheric air which has not been dried ultra-violet rays produce H_2O_2 , ozone, and the anhydride of nitrous acid, the last in very small quantities. These oxidising agents can readily be detected by chemical methods.

Equilibrium $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + \text{Na}_2\text{SO}_4$.—W. Herz.—The average value of the quotient, $\frac{\text{Na}_2\text{CO}_3}{\text{Na}_2\text{SO}_4}$, in the above transposition is about 0.054 , which is considerably higher than would be expected from the solubilities of CaSO_4 and CaCO_3 . Probably double salts are formed during the transposition.

MISCELLANEOUS.

Oxythiophenes.—Maurice Lanfry.—When hydrogen peroxide acts on thiophene the products differ according to the proportion of active oxygen present. If it exceeds 1.5 gm. per 1 gm. of thiophene, d'oxy- and tetroxy-thiophenes are formed. If the proportion is lower, a mixture of substances is obtained, but the author has not succeeded in separating and identifying them. Possibly they are polymers of monoxy- and dioxythiophene. If concentrated hydrogen peroxide is employed no oxythiophenes are formed.—*Comptes Rendus*, cxiii., No. 1.

Iron and Steel Institute, Autumn Meeting, October 5th, 1911.—Circumstances have arisen which have unfortunately led to the abandonment of the arrangements made to hold the Autumn Meeting of the Iron and Steel Institute in Turin. Arrangements have therefore been made for the Autumn Meeting to be held (by kind permission) at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday, October 5th, at 10.30 a.m. It is necessary the meeting will be resumed in the afternoon. The following is the list of papers which have been submitted, a selection of which will be read and discussed:—

"Reports on the Iron Ore Resources of Italy."

(a) Sardinia, by Ing. L. Testa.

(b) Brembana Valley, by Cav. G. Calvi.

(c) Central Italy, by Ing. A. Ciampi.

(d) Southern Italy and the Island Dependencies, by Prof. G. la Valle.

"Temperature Influences on Carbon and Iron," by E. Adamson (Sheffield).

"Mechanical Influence of Carbon on Alloys of Iron and Manganese," by Prof. J. O. Arnold (Sheffield) and F. K. Knowles (Sheffield).

"Autogenous Welding of Metals," by Dr. Francesco Carnevali (Turin).

"Application of Electric Energy to the Manufacture of Iron and Steel in Italy," by Cav. Ing. Remo Catani (Rome).

"Present State of the Metallurgical Industry of Italy," by Signor Comm. Luigi Dompé and Cav. Francesco Saverio Pucci (Milan).

"Origin of the Iron Ores of Swedish Lapland," by L. L. Fermor (Culcutta).

"New Industrial Processes for the Cementation of Steel," by Cav. Prof. Dr. Federico Giolitti (Turin).

"Cementation with Gas under Pressure," by Prof. Dr. F. Giolitti and Dr. Francesco Carnevali (Turin).

"Transformation of Steel within the Limits of Temperature employed for Heat Treatment," by L. Grenet (Argenteuil, France).

"Researches on the Nature of the Phosphates contained in Basic Slag derived from the Thomas Gilchrist Dephosphorisation Process," by Victor Adolphe Kroll (Luxembourg).

Regulations for the Smelting of Materials containing Lead, the Manufacture of Red or Orange-lead, and the Manufacture of Flaked Litharge (Factory and Workshop Act, 1901).—The Chief Inspector of Factories has forwarded a copy of the Regulations as above, made by the Secretary of State on August 12th, 1911, together with a Memorandum, explaining certain of the requirements. The Regulations, based upon the Report of Dr. E. L. Collis, Medical Inspector of Factories, were issued in draft in February, 1911 ("Special Report on Dangerous or Injurious Processes in the Smelting of Materials containing Lead, and in the Manufacture of Red and Orange-lead and Flaked Litharge," Wyman and Sons, Ltd., London). The objections received were considered by the Secretary of State, and an amended draft was issued in May, 1911, to which no objections, other than those subsequently withdrawn, were made. The Regulations apply automatically to all works in which the processes named above are carried on, and come into force on October 1st, 1911, except that so much of Regulations 2 and 3 as requires provision of efficient exhaust draught is deferred until May 1st, 1912. They supersede the existing Special Rules for Lead Smelting and for the Manufacture of Red and Orange-lead and Yellow Lead. The Special Rules for the Manufacture of White Lead are unaffected by the new code; both codes may be in force in the same works, each being limited, however, to the particular manufacture concerned. The following are the principal points on which the Regulations differ from the draft of February, 1911:—1. Extension of time as regards the exhaust ventilation required by Regs. 2 and 3. 2. Modification of the definition of "lead material" so as to exempt zinc ore, and material resulting from the treatment thereof, containing less than 2 per cent of lead. Sulphide ores, therefore, it should be noted, are exempted only prior to calcination. 3. A proviso has been added to Reg. 2 allowing lead material to be moved to a furnace by persons wearing suitable respirators when damping, exhaust ventilation, and enclosing, so as to prevent the escape of dust, are none of them practicable. 4. Under Reg. 5 as modified, the use of a covered receptacle in removal of lead material from the exhaust draught is only required if vapour containing lead is given off.

THE CHEMICAL NEWS.

VOL. CIV., No. 2706.

ACTION OF RADIUM EMANATION ON THORIUM SALTS.

By M. HERSCHFINKEL.

Two years ago Sir William Ramsay and Usher (*Ramsay, Journ. Chem. Soc.*, xcv., 624; *Ramsay and Usher, Ber.*, xlii., 2930) showed that when a solution of thorium nitrate is allowed to stand for some months, a certain amount of carbon dioxide is set free (0.58 to 1.2 cc. from a solution containing 270 grms. of salt), and that if the same thorium salt is subjected to the action of radium emanation there is an even more rapid production of similar amounts of carbon dioxide (about 0.5 cc. when the radium emanation in equilibrium with about 0.2 gm. of radium acts on 270 grms. of thorium nitrate). All the elements of the same group (Si, Zr, Ti), as well as thorium, yield carbon dioxide under the action of radium emanation, but the quantity of gas set free is not so large. The action of the emanation on other salts— $\text{Hg}(\text{NO}_3)_2$, 300 grms.—gave only a very small volume of CO_2 .

In order to explain this result, Ramsay and Usher suggested that the carbon of the carbon dioxide formed resulted from the transformation of the atoms of the thorium group by the radium emanation. Now it is already known that in presence of the emanation organic matter is very readily oxidised, giving carbon dioxide (M^{me}. Curie, "Traité de Radioactivité").

Hence it was necessary to repeat Ramsay's experiments, and to find out if the evolution of carbon dioxide could be due to the presence of small quantities of organic impurities in the salts employed.

I performed various experiments with thorium nitrate, and I am deeply grateful to M^{me}. Curie for having put at my disposal the large quantities of radium emanation used in my experiments which were carried out in her laboratory.

The apparatus which I used and which will be described fully in a more detailed notice, enabled me to bring together the thorium nitrate and the emanation, avoiding any contact with the stopcocks, from the grease of which the carbon dioxide might be produced. The apparatus was carefully cleaned with chromic mixture.

The emanation was produced by a solution containing about 3 dgms. of radium chloride. It was carefully purified and freed from any trace of carbon dioxide. The thorium nitrate was specially purified by the firm of Merck in order to remove as far as possible any organic impurities.

The different operations which were carried out to extract the gas from the apparatus did not cause an appreciable loss of any carbon dioxide which might be present. For instance, 0.1 cc. of CO_2 could be introduced and then readily detected in the gas extracted from the apparatus.

In the first experiment a large quantity of emanation was directed on to a considerable amount of thorium nitrate. When most of the emanation, which was always in contact with the thorium nitrate, had been destroyed the gas contained in the apparatus was analysed.

In order to extract the gas from the apparatus the thorium solution was warmed, and simultaneously detonating gas obtained by the electrolysis of water was bubbled through it. The gas was then introduced into a eudiometer, where the detonating gas was re-combined, and the carbon dioxide was then converted into the monoxide by the action of a spark in presence of phosphorus. The nitrogenous compounds which were sure to be present in the gas were absorbed by mercury after the action of the spark in presence of oxygen.

The carbon monoxide was then determined by Nicloux's method (action on iodic acid with production of iodine). Finally, the presence of carbon dioxide was detected by the production of a pink colouration of the solution of iodine in carbon disulphide.

When the emanation in equilibrium with 0.1 gm. of radium acts on 125 grms. of thorium nitrate for twelve days about 1 cc. of carbon dioxide is obtained. If the thorium solution stands for the same length of time without the emanation it yields only a trace of carbon dioxide. If the thorium salt is replaced by distilled water the emanation gives only a little carbon dioxide (0.1 cc.).

If the action of the emanation is not an atomic transformation but an oxidation phenomenon, another oxidising agent, such as potassium permanganate, would also give carbon dioxide with thorium nitrate; i.e., with its organic impurity. To the solution of thorium nitrate I added a small quantity of potassium permanganate, meanwhile cooling so that the action did not commence too soon. I obtained thus larger quantities of carbon dioxide than with the emanation.

Hence we must conclude that the carbon dioxide, which is formed in the thorium with the emanation, is not due to an atomic transformation of thorium into carbon. In any case the production of carbon dioxide observed by Sir William Ramsay is no proof of this transformation, since an oxidising agent also gives carbon dioxide.

The impurity in the salt of thorium is very probably a trace of oxalic acid which is employed in preparing it.

It seems probable to me that the liberation of carbon dioxide in the case of other substances could be proved to be due to an analogous cause.—*Comptes Rendus*, cliii., 255.

EUROPIUM.

By C. JAMES and J. E. ROBINSON.

By fractionally crystallising the nitrates of a mixture of the rare earths, very rich in samarium and gadolinium, from concentrated nitric acid, Demarçay (*Comptes Rendus*, cxvii., 728) obtained a new nitrate more soluble than gadolinium and less soluble than samarium. This element, which differed from all the rare earths by its characteristic spectrum, he provisionally named Σ .

In 1900 (*Comptes Rendus*, cxxx., 22) the discoverer obtained this earth in a purer condition, and found that the oxide was white with a pink tinge. The salts were of a pale rose colour, and gave the following absorption spectrum:—590, 570, 535, 525, 465, 395.5, 385.5, 380.5. None of these bands was strong, however. A year later Demarçay (*Comptes Rendus*, cxxvii., 24) obtained the element in a fairly pure condition, and named it europium. He also found that the crystallisation of the double magnesium nitrate gave a more rapid separation.

Some years previous to Demarçay's work, Lecoq de Boisbaudran (*Comptes Rendus*, cxiv., 575) had observed three lines in certain samarium solutions, which did not occur in Cleve's pure material. These lines were later found to coincide with those given by europium.

Crookes, during his magnificent work upon the phosphorescent spectra, discovered a new spectrum, which, as recent work shows, was due to europium.

Urban and Lacombe (*Comptes Rendus*, cxxxviii., 628) showed that isomorphous bismuth magnesium nitrate came between samarium and europium with regard to its solubility in fairly strong nitric acid. This method enabled them to obtain several grms. of europium, in a very pure condition from a comparatively large amount of samarium and gadolinium (610 grms. oxides).

In order to obtain a sufficient quantity of this earth for further study, the writers worked up very large amounts of material. This material comprised the following:—Oxides from insoluble double sodium sulphates from about 200 kilos. of yttrium minerals; all the samarium and gadolinium

oxides derived from about 200 kilos. of Brazilian monazite; and about 110 kilos. of oxides obtained from the more soluble double potassium sulphates coming from very large amounts of Carolina monazite.

These crude oxides were first converted into double magnesium nitrates in the following manner:—Concentrated nitric acid and the oxides were gradually mixed in a large porcelain dish, care being taken not to allow the liquid to become alkaline. All cerium in the ceric condition was reduced by addition of rare earth oxalates of similar metallic content to the oxides. About two bottles of concentrated nitric acid were used in each batch. The solution was finally made as nearly neutral as possible, poured into a large earthenware vessel and allowed to stand until it became clear. This operation took about twelve hours. An equal amount of acid was neutralised with crude magnesium oxide. The magnesium nitrate solution was made slightly basic by heating with a little more of the oxide. The precipitate of iron and aluminium hydroxides was then filtered off. The filtrate was acidified and mixed with the rare earth nitrate solution. The mixed liquids were evaporated until such a concentration was obtained that half of the material separated out in a crystalline state upon cooling. The mother-liquor was poured off and evaporated further. The double nitrates that separated were re-crystallised three times, after which they were drained and placed aside. When the mother-liquors began to crystallise badly, owing to increase in the impurities, they were diluted and precipitated with oxalic acid. The oxalates were filtered off on large Büchner funnels, thoroughly washed with water, and ignited in fire-clay crucibles placed in a large furnace.

The oxides obtained in the above manner contained small quantities of lanthanum, cerium, and praseodymium, large quantities of neodymium, and fair amounts of samarium, gadolinium, and yttrium earths. This material was converted into the double magnesium nitrate in a similar way, as described above, with the exception that pure magnesium oxide was used. These double magnesium nitrates were fractionally crystallised according to the usual method with 30 per cent nitric acid as the solvent. After the crystallisation had proceeded for a short time it was found that the neodymium, lanthanum, cerium, and praseodymium rapidly collected in the least soluble portion. The intermediate fractions consisted chiefly of the pale yellow samarium compound, while the most soluble portions were rich in gadolinium, and were coloured very pale pink by the erbium metals. As soon as the crystals of the simple nitrates of the yttrium elements made their appearance it was deemed advisable to commence the addition of the isomorphous bismuth magnesium nitrate. Five kilos. of bismuth were converted into the double nitrate. This salt was added in portions of about 1 kilo. to the most soluble fraction, such procedure rapidly eliminating all traces of samarium and europium. When the yttrium earths were entirely freed from samarium and europium, they were separated from the series.

With regard to the yttrium earths, it was found that erbium and yttrium separated first, holmium next, and lastly dysprosium and terbium. It proved to be practically impossible to free gadolinium entirely from terbium by the magnesium nitrate method. A crystallisation of the simple nitrates caused yttrium, erbium, holmium, and dysprosium to pass rapidly into the most soluble part.

The fractions containing lanthanum, cerium, praseodymium, and neodymium were set aside as soon as they were freed from all traces of samarium. Samarium was gradually removed after a large number of crystallisations, at which time it was considered certain that all europium had passed further along the series.

These operations were carried out in very large porcelain dishes. As these dishes were uncovered, the top crystals deliquesced, causing the samarium to pass beyond its correct position in the series. Because of this difficulty, and since the fractions had decreased in bulk considerably, the series was removed from the dishes and placed in

casseroles, which were covered with large watch-glasses. From now on the solvent used was nitric acid of about 50 per cent concentration. Hitherto the only visible sign of europium was a fine sharp absorption band in the blue, shown by the gadolinium fractions next to samarium.

As the work proceeded, the europium band was observed to become stronger in the fractions between samarium and gadolinium. Later the two bands in the green made their appearance. The fractions kept getting smaller and smaller, since all mother-liquors that gave no europium absorption had been removed. At this period nearly all the samarium had been separated. After continuing the work a little longer the fractions, which consisted almost entirely of bismuth magnesium nitrate, were mixed according to their absorption spectra. The liquids were diluted, precipitated with hydrogen sulphide, and filtered. The filtrate was precipitated with oxalic acid and the europium oxalate filtered off and washed. About 100 grms. of this compound were obtained. Each precipitate was then ignited to the oxide, the oxide dissolved in nitric acid, and the resulting solution tested with the spectroscope. The solutions of the europium material nearest to the samarium were found to be still slightly contaminated with that element.

It was decided to submit the whole material to more series of crystallisations. For this purpose it was again converted back to the double magnesium nitrate and mixed with bismuth magnesium nitrate. When the europium was found to be free from samarium it was dissolved in water, saturated with hydrogen sulphide, and the clear filtrate was once again precipitated with oxalic acid. This europium oxalate was then washed, dried, and stored for the study of its compounds.

In this work, which required two years, about 30 kilograms of the crude double nitrates of samarium and gadolinium were extracted and fractionated. About 5 kilograms of pure samarium oxalate and about 4 kilograms of nearly pure gadolinium oxalate were prepared.

The authors hope to publish the second part of this paper in the near future.

Durham, N.H., June 9, 1911.

ON THE REPORT OF THE CORROSION COMMITTEE OF THE BRITISH ASSOCIATION, 1911.

By J. NEWTON FRIEND.

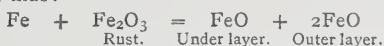
THE Report of the Corrosion Committee of the British Association for this year, appearing in the *CHEMICAL NEWS* for September 22 and 29 (vol. civ., pp. 142, 155), will be heartily welcomed by all persons interested in questions pertaining to corrosion. A consideration of the curves shown in Figs. 1 and 2 of the Report will suffice to show how different were the relative corrosions of the metals when sea-water was used from when sulphuric acid was employed as the corroding medium. This is an observation of unusual importance in view of the fact that the so-called "acceleration tests" for determining the resistance of iron and steel towards corrosion are usually made by immersing the metals in sulphuric acid of various concentrations, the losses in weight being determined. It is then assumed that the metal which resists the attack of the acid most successfully will likewise resist other corrosive influences, such as those of the atmosphere, sea- and river-waters, &c., the best. In my recent book entitled "The Corrosion of Iron and Steel" (Longmans, 1911, p. 273) I have shown, from theoretical considerations, that acceleration tests conducted with acids cannot be expected to give the same results as prolonged exposure to other corroding influences, and that these tests are therefore unreliable. Hitherto the chief practical confirmation of this has been the research of Frazer, published in the *Journal of the West of Scotland Iron and Steel Institute* in 1907. It is gratifying to learn that the results

of the Corrosion Committee bear out the same conclusions. Frazier showed conclusively that, whereas acid and basic steels corroded at practically identical rates in air, fresh water, and brine, the basic metal was some *five times* as resistant toward acid attack as the acid steel.

Attention is drawn to the fact that the deposits on the corroded bars after exposure to sea-water were made up of two different types, namely, light brown rust and a bluish black layer underlying the above. This is a very ordinary observation, and characterises the style of corrosion usually met with in cases where the metal is completely submerged in water, provided the whole of the metal has not undergone corrosion. The explanation is not far to seek. The rusting of iron under water takes place in three stages, namely:—

1. The solution of the metal to form a ferrous salt.
2. The decomposition of the ferrous salt with the formation of ferrous oxide or a basic insoluble salt.
3. The oxidation of the ferrous oxide to brown rust.

When completely immersed in water, reactions 1, 2, and 3 proceed fairly rapidly at first, and an outer layer of brown rust is produced. But as time progresses it becomes increasingly difficult for oxygen to pass through the layers of adhering oxide to the metal; the latter therefore becomes oxidised to the ferrous condition at the expense of the rust around it, thus:—



(For the sake of simplicity the rust is assumed to be Fe_2O_3 , and the catalytic action of the necessary traces of electrolyte omitted).

The ferrous oxide thus produced from the iron constitutes the under layer of dark blue hue described in the Report. The outer layers of ferrous oxide obtained by the reduction of the rust are simultaneously oxidised to rust again by the oxygen diffusing towards them. This process will continue all the time the metal is under the water. The thicker the layer of ferrous oxide, the slower will the metal corrode; hence an explanation is to hand for the well-known fact that the metal corrodes more rapidly at first than later. Further, the deeper the metal is immersed in the water the slower is the rate of diffusion of the oxygen in the air to it. Hence the greater the proportion of ferrous oxide on the corroded metal.

It is a pity that no details are given as to the method of experimentation. Possibly, however, the authors will remedy this omission in later Reports. It is important to know if the metal lay in contact with the walls and sides of the containing vessel, or if the bars were suspended from hooks, &c. Also, the nature of the composition of the containing vessels should be given. If they were glass, and thus translucent or transparent to light, the proportion of ferrous oxide to ferric oxide would probably be less than if the vessels were of earthenware and opaque. Details such as these should always be given, as, in their absence, much excellent work is rendered less valuable owing to the difficulty of comparing it with other work of a similar nature. Furthermore, if details are not given, any sources of error are less likely to be discovered, and the difficulties of accounting for anomalous results greatly enhanced.

It is a pity that the Report should begin with such a careless statement as "despite the fact, however, that the modern metallurgy of iron and steel largely centres about the influence of various alloying elements upon its physical and mechanical properties, *no reliable data are available as to the influence exerted by them upon its corrodibility.*" Surely the Committee is not unaware of the monumental researches of Diegel and others upon these very lines! Surely, too, if they were, they would not class their results as "unreliable data." Presumably this is merely a slip of the pen; but it is none the less regrettable in that it gives an undue sense of importance to the work done by the Committee, and a false impression as to the actual state of the world's knowledge (or, shall we say, *published data*) on the point.

THE MELTING-POINTS OF THE CHEMICAL ELEMENTS.

By GEORGE K. BURGESS, U.S. Bureau of Standards.

THERE has been much work done recently in the more exact location of some of these fixed points. The accompanying table represents an attempt to assign the most probable values to the several melting-points from a consideration of all the data available, and is a revision of the list in the new Smithsonian *Physical Tables*.

In so far as possible, the values are reduced to a common temperature scale, that given by the gas thermometer. In general, differences between the various gas scales as recently determined and the thermodynamic scale are less than the uncertainties of reproducibility by any one method. For example, the four observations on the melting-point of gold, by the constant volume nitrogen thermometer, published within the past ten years, range from 1059.3° to 1067.2°C. , and the correction to the thermodynamic scale is here 1° or less. Besides the direct gas thermometer determinations, there are, also, for many of the melting-points, precise differential checks made by electrical resistance, thermo-electric, or optical thermometers. The difference between the melting-points of gold and copper is thus known to be 20°C. by auxiliary methods more closely than these temperatures have usually been independently located by the gas thermometer.

For the range 100° to 500°C. , the scale here adopted agrees with the value 444.7 for the sulphur boiling-point, a temperature that has been many times determined, and which is perhaps the best known fixed point above 300° .

For high temperatures the scale is satisfied very exactly by taking $c_2 = 14,500$ in the formula for Wien's law connecting I , monochromatic luminous intensity, and T , absolute temperature: $\log I/I_1 = c_2 \lambda \log e (1/T_1 - 1/T)$. This agrees well with the gas thermometer measurements of Day and Sosman in the range 1000° to 1550°C. The use of Wien's law possesses the theoretical advantage for extrapolation beyond 1550° in giving the thermodynamic scale.

In the table, elements whose melting-points are well known or used as standards are printed in capitals. An idea of the exactness of our knowledge of some of the melting-points is also given.

Melting-points (C.) of the Chemical Elements.

Element.	Melting-point.	Remarks.
Helium ..	$< -269?$	B.-p. He = -268.5° . Kammerlingh-Onnes
Hydrogen ..	-259	Travers-Jaquered
Neon ..	$-253?$	
Oxygen ..	$-230?$	Range -227 to -235
Fluorine ..	-223	Moissan-Dewar
Nitrogen ..	-210.5	Fischer-Alt
Argon ..	-188	Ramsay-Travers
Krypton ..	-169	Ramsay-Travers
Xenon ..	-140	Ramsay-Travers
Chlorine ..	-101.5	Johnson-McIntosh
MERCURY ..	38.7 ± 0.5	
Bromine ..	-7.3	Range -7.5 to -7.0
Cæsium ..	26	Range 25.3 to 26.5
Gallium ..	30.1	Lecoq Boisbaudran
Rubidium ..	38	Range 37.8 to 38.5
Phosphorus ..	44.1	Hulett
POTASSIUM ..	62.3 ± 0.2	
Sodium ..	97.5 ± 1.0	
Iodine ..	114 ± 1	
Sulphur ..	113.5 to 119.5	Various forms
Indium ..	154.5 ± 0.5	
Lithium ..	186	Kahlbaum
Selenium ..	217 to 220	Various forms. Saunders
Tin ..	231.9 ± 0.2	
Bismuth ..	270	Range 267.5 to 271.5
Thallium ..	302 ± 1	
CADMIUM ..	321.0 ± 0.2	Range 320.0 to 321.7

Element.	Melting-point.	Remarks.
LEAD	327.4 ± 0.4	Range 418.2 to 419.4
ZINC	419.3 ± 0.3	
Tellurium ..	451 ± 1	
Arsenic	500	Guntz-Broniewski
ANTIMONY ..	630 ± 1	"Kahlbaum" purity only
Cerium	645 ?	
Magnesium ..	650 ± 2	
ALUMINIUM ..	658 ± 1	
Calcium	805 ± 5	
Lanthanum ..	810 ?	Muthmann-Weiss
Strontium ..	>Ca, <Ba ?	
Neodymium ..	840 ?	Muthmann-Weiss
Barium	850	Guntz
Germanium ..	<Ag	Winkler
Praseodymium	940 ?	Muthmann-Weiss
SILVER	961 ± 2	
Radium	600 to 1200 ?	Unknown
GOLD	1063 ± 3	
COPPER	1083 ± 3	
Manganese ..	1225 ± 15	
Yttrium	1000 to 1400 ?	Unknown
Samarium ..	1300 to 1400	Muthmann-Weiss
Scandium ..	1000 to 1400 ?	Unknown
Silicon	1420 ± 15	
NICKEL	1450 ± 10	Day-Sosman = 1452
Cobalt	1490	Day-Sosman
Chromium ..	1505 ± 15	
IRON	1520 ± 15	
PALLADIUM ..	1550 ± 15	Day-Sosman = 1549
Zirconium ..	>Silicon	Troost
Thorium	>1700, <Pt	Wartenberg
Vanadium ..	1730 ± 30	
PLATINUM ..	1755 ± 20	Waidner-Burgess = 1753
Beryllium ..	>1800	Parsons
Ytterbium ..	1600 to 2000 ?	Unknown
Titanium ..	2200 to 2400 ?	Weiss-Kaiser
	1800 to 1850	Hunter
Rhodium ..	1920 ?	Range 1907 to 1970
Ruthenium ..	>1950	July
Niobium ..	2200 ?	v. Bolton = 1950
Boron	2200 to 2500	Weintraub
Iridium	2300 ?	Range 2100 to 2350
Uranium	near Mo	Moissan
Molybdenum ..	2500 ?	Range 2110 to >2500
Osmium	2700 ?	Waidner-Burgess
Tantalum ..	2900	Waidner-Burgess
TUNGSTEN ..	3000 ± 100	Range 2575 to 3250
		Waidner-Burgess = 3080
Carbon	?	Unknown

—*Journal of the Washington Academy of Sciences*, No. 1.

THE INFLUENCE OF CONSTITUTION ON THE MOLECULAR VOLUMES OF ORGANIC COMPOUNDS AT THE BOILING-POINT.*

By GERVAISE LE BAS, B.Sc.

(Continued from p. 153).

Other Constitutive Influences.

It is now necessary to remark that besides the indirect action of two separated atoms in a chain by means of the valencies, there is possibly another and direct action by means of residual affinity. This is not possible in the normal hydrocarbon chain, but this class of constitutive effect is found to be very probable by studying the molecular volumes of compounds which illustrate other arrangements. It is considered to be even possible to arrive at a knowledge of the configuration of the molecules by a close consideration of their molecular volumes in the light of this hypothesis.

* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

The Effect of Branching the Hydrocarbon Chain.

It is well known that the presence of the iso-group in a compound greatly affects the boiling-point and other physical properties, such as the molecular volume. So far as the latter is concerned, nearly all the data relate to iso-compounds, and these are scanty. Hence it is not possible to draw any very general conclusions. It is known, however, that in the paraffin and other series the secondary and tertiary compounds possess lower boiling-points and smaller molecular volumes than the normal members of the series. A few exceptions, such as the fatty acids and the halogen derivatives of the paraffins, occur—which seem to show that the precise nature of the effect is dependent to some extent on the nature of the distinguishing element or group of the series. Still, in the paraffin series, where other and complicating constitutive effects are likely to be absent, the branching of the chain involves a diminution in the volume. The following important generalisation as regards the boiling-points of the compounds is significant:—

The boiling-point of a compound is smaller the more a hydrocarbon chain becomes branched, and tends to a minimum when the form of a molecule approaches that of a sphere.

This rule of Naumann, if taken in conjunction with the tendency of the branched paraffins to show diminished volumes, strongly points to the fact that compactness of structure tends to increase the affinity pressures exerted on the atoms, and thus to diminish the volumes. If this is due to the interaction between the subsidiary chains by reason of the residual affinity with which we may suppose they are endowed, then there should be a weakening of the intermolecular forces with a consequent depression of the boiling-point. This is what we find.

Some of the accurate data which Young has obtained at the critical-point are rather interesting, and though the evidence taken by itself may not be of much weight, yet if taken in conjunction with other facts to be immediately given may be important.

The figures refer to a comparison between the volumes of certain normal compounds with corresponding mono- and di- iso derivatives.

Compound.	M.V.	Δ.	Skeleton.
n-Pentane, C ₅ H ₁₂ ..	309.7	-2.6	C—C—C—C—C
Isopentane, C ₅ H ₁₂ ..	307.1		$\begin{array}{c} \text{C} \\ \diagup \end{array}$ C—C—C
Methyl butyrate ..	340.0	-1.4	C—C—C—COOC
C ₃ H ₁₀ O ₂ ..			$\begin{array}{c} \text{C} \\ \diagup \end{array}$ C—COOC
Methyl isobutyrate ..	338.6	-10.0	C—C—C—C—C—C
n-Hexane, C ₆ H ₁₄ ..	366.5		$\begin{array}{cc} \text{C} & \text{C} \\ & \\ \text{C} & -\text{C} \\ & \\ \text{C} & \text{C} \end{array}$
Di-isopropyl, C ₆ H ₁₄ ..	356.5	-7.0	C.C.C.C.C.C.C
n-Octane, C ₈ H ₁₈ ..	488.6		$\begin{array}{cc} \text{C} & \text{C} \\ & \\ \text{C} & -\text{C} - \text{C} - \text{C} \\ & \\ \text{C} & \text{C} \end{array}$
Di-isobutyl, C ₈ H ₁₈ ..	481.6		

It is to be observed that although the two simple iso-compounds show contractions of about the same order of magnitude, the contractions for the di- iso-compounds are very much larger, larger indeed than twice the value for one iso-group.

An accumulation of iso-groups thus increases the contractions greatly.

Another point to notice is that the compound di isopropyl

shows a considerably larger contraction than for di-isobutyl and possibly for di-isoamyl. It may thus be supposed that an approximation of the pair of methyl groups greatly increases the contraction, but when they become sufficiently separated this value possibly sinks to twice 2.6 or -5.2. So far as it goes this is evidence in favour of interaction of the groups owing to residual affinity. Owing to symmetry curvature of the carbon chain cannot be supposed.

The Symmetrical and Unsymmetrical Esters and Ethers.

It is one of the permanent achievements of the older work to have shown that the unsymmetrical ethers (Döbriner) and the monocarboxylic esters (Gartenmeister) possess smaller volumes than those of the corresponding symmetrical compounds.

It can be shown that the volumes of the latter exactly correspond with those of a normal series like the paraffins. The same is true of such compounds as acetic and propionic anhydrides. For this reason we write the formulæ in the same manner as those of the normal paraffins, viz., like a straight chain.

CH₃.CH₂.CH₂.CH₂.CH₂.CH₂.CH₃ Normal heptane.
CH₃.CH₂.CH₂.O.CH₂.CH₂.CH₃.. Dipropyl ether.
CH₃.CH₂.CO.O.CH₂.CH₂.CH₃.. Propyl propionate.
CH₃.CH₂.CO.O.CO.CH₂.CH₃.. Propionic anhydride.

The unsymmetrical compounds may, however, be written like the secondary compounds, the iso-paraffins:—

CH₃
|
CH₃>CH—CH₂—CH₂—CH₃.. Iso-hexane.
CH₃.CH₂.CH₂
|
CH₃>O Methyl propyl ether.
CH₃.CH₂.CH₂.CO
|
CH₃>O Methyl butyrate.
(To be continued)

A STUDY ON THE
PHENOLSULPHONIC ACID METHOD FOR THE
DETERMINATION OF NITRATES IN WATER.*

THE CHIEF SOURCES OF ERROR IN THE METHOD.

By E. M. CHAMOT, D. S. PRATT, and H. W. REDFIELD
(Concluded from p. 161).

IX. Errors Due to the Presence of Chlorides in the Residue.

WHEN a water contains a large amount of chlorine as chlorides, the nitric nitrogen determined by the phenolsulphonic acid method is much too low. This error has been long recognised, but it is not until very recently that it has been shown that even small amounts of chlorides may cause a most serious error. As long ago as 1891 Bartram called attention to the fact that the age of the reagent had an important bearing upon the magnitude of this error (*Journ. Frank. Inst.*, 1891, cxxxi., 385); with a freshly prepared reagent there was little apparent loss, but the same reagent after it had aged furnished results lower than before. This variation in behaviour we now know to be due to the gradual change of mono acids into the disulphonic acid.

The low results obtained when a water residue contains chlorides are partially due to mechanical loss and in part due to interaction of the hydrochloric and nitric acids liberated. This was proved by proceeding in the manner already described under the losses due to carbonates. While the investigation was in progress, Farcy arrived at similar results by substantially similar methods (*Bull. Soc. Chim.*, 1909, [4], v., 1091). Lombard and Laport had already advanced a similar hypothesis without experimental data (*Bull. Soc. Chim.*, 1909, [4], v., 321). Farcy has

also shown that bromides and iodides introduce a similar error (*Bull. Soc. Chim.*, 1909, [4], v., 178, 563). Determinations were made by this author and by Perrier and Farcy of the losses in nitric nitrogen when more than six parts per million of chlorine as chloride were present. The data published show a striking regularity in the proportion of loss to halogen present. The proportional increase in loss with the increase in halogen is such that a correction for error would be possible. But Stewart and Greaves obtained no such proportional regularities (*Journ. Am. Chem. Soc.*, 1910, xxxii., 756). We had already arrived at a similar result. The loss in nitrogen increases with the amount of chlorides present, but the per cent of loss is so very irregular that it was not possible to adopt any numerical correction. The more mono acid the reagent contained the greater the variation in the nature of the loss. Even when a reagent containing no mono acids is employed the amount of loss is too irregular with below 10 parts per million of chlorine to permit of correction, but with over 10 parts of chlorine the loss approximates 30 per cent of the nitric nitrogen. Space forbids the incorporation here of more than one series of experiments by way of illustration. In the table given each water residue contained 10 parts per million of nitrogen as nitrate and the amount of chlorine as chloride indicated. In each case the limits given are from the results of at least five different water residues and in several instances many more. Comparisons were made with a pure tripotassium nitrophenolsulphonate standard.

Parts per million of chlorine present.	Parts per million of N found.	
	Minimum.	Maximum.
0	10	10
0.5	9.35	9.75
1	9.25	9.85
2	8.50	8.75
3	8.30	8.75
4	7.80	8.45
5	7.65	7.80
10	7.20	7.45
15	7.20	7.30
20	7.05	7.35

It appears, therefore, that the method of procedure for the prevention of error, consisting in the addition of a like quantity of chlorides to the standard as has been determined in the sample, is not always safe and is applicable only when over 10 parts per million of chlorine are present. When accurate results are required, the halogens must be removed by means of silver sulphate.

Silver compounds have long been employed for the removal of chlorine and prevention of loss. Shaking the sample with silver sulphate is at the present time the method in general use. Shaking with silver oxide has also been suggested (Tatlock and Thompson, *Chem. Ind.*, 1904, xxiii., 428), but neither process is satisfactory. Marcille advocates using an ammoniacal solution of known strength (*Ann. Chim. Anal.*, 1909, xiv., 303), evaporating to dryness, adding the sulphonic acid, diluting as usual, and adding ammonium hydroxide to develop the colour, and dissolve the silver chloride formed. This method has given in our hands perfectly satisfactory results, but is objectional in a water analysis laboratory because of the ammonia fumes evolved. The procedure which has given us the best results and eliminates ammonia consists in determining the chlorine present in the sample, then adding to the volume of the sample to be used for the determination of nitrates such a volume of a solution of silver sulphate as will remove all but about 0.5 of a part per million of chlorine, heating to boiling, adding a little "aluminium cream" to aid in clarifying and to remove colour, filtering and evaporating to dryness on the water-bath: the residue is then treated with sulphonic acid as usual. As thus practised the method becomes very little longer than without the removal of chlorides, and requires substantially no more time than that of Marcille.

* From the *Journal of the American Chemical Society*, xxiii., No. 3.

X. *Errors Due to the Presence of Iron* (Drown and Hazen, "Purification of Water and Sewage," Special Report, Massachusetts State Board of Health, 1870, p. 712).

When dealing with ferruginous waters very high in iron a residue is obtained which is penetrated only with great difficulty by the sulphonic acid reagent. The results obtained, therefore, show great variations. These variations are not, however, in proportion to the iron present. With the standard or Gill reagent the losses in nitrogen are sometimes very great, but it was found that when the reagent is of such composition as to permit heating in contact with the residue for a few minutes no such discrepancies can be detected. Should the composition of the reagent preclude heating with the residue the iron must be removed.

The effect of the presence of iron was tried on many samples of water containing up to 5 parts per million of Fe.

When much iron is present, and the alkali used for the development of the colour is added very slowly, a red or brown solution is obtained whose colour is destroyed by the addition of a slight excess of alkali with the formation of a precipitate of iron hydroxide and the usual yellow colour of the nitrophenoldisulphonate. The red coloration may thus serve as an indication of the presence of much iron, and as a warning that losses of nitrogen may be expected unless the contact of reagent and residue has been unusually intimate.

XI. *Errors Due to other Interfering Inorganic Substances.*

Both nitrites and magnesium compounds have been stated at various times to introduce errors of sufficient magnitude to necessitate special treatment of the water.

To test the influence of nitrites, nitrate-free silver nitrite was prepared, decomposed by pure sodium chloride, and the resulting sodium nitrite employed.

A large number of water residues containing known added amounts of pure sodium nitrite but no nitrates were treated with the sulphonic acid reagent as usual. It was found that nitrites in amount less than 0.2 part per million of nitrogen gave no yellow colour, and therefore had no influence upon the determination, but if present in excess of this value the amount of nitric nitrogen is found too high, apparently due to a higher oxidation of part of the nitrogen in the nitrite.

According to Pouget this oxidation takes place in accordance with the equation $3\text{HNO}_2 = 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$ (*Bull. Soc. Chim.*, 1910, vii., 449), and is quantitative for amounts of nitrite from 0.1 to 0.3 mgrm. In the case of nitrites present in water residues, however, we have obtained yields of nitric nitrogen always much below that indicated by this equation, and it is not until the nitrogen reached 1 part per million that the final yellow colour was of sufficient intensity to appreciably affect colorimeter readings.

Waters very high in magnesium compounds yield residues whose particles, as in the case of iron compounds, are penetrated only with great difficulty by the sulphonic acid reagent, and it appears that the difficulty lies in failure to obtain intimate contact between reagent and nitrate. Very thorough rubbing with a glass rod is essential. The chief error when dealing with waters high in magnesium chloride is due to the effect of the chlorine and not of the base.

Summary.

1. Sulphonic acid reagents containing mono acids are subject to change with age, and yield results greatly affected by temperature, concentration, variation in character of alkali, &c. They cannot be satisfactorily employed with permanent standards.

2. In order that accurate results may be obtained chlorides, carbonates, and organic matter must be removed.

3. Nitrites present in small amount do not appreciably affect the final results, but when exceptionally high must be destroyed or corrected for.

4. A sulphonic acid reagent of definite composition should be used. Such a reagent is described in a succeeding paper.

COMPARISON OF METHODS FOR THE DETERMINATION OF NICKEL IN STEEL.

By JAMES J. BOYLE.

HAVING noticed that many discrepancies occur in determining nickel in steel by the old ether separation method, and the subsequent precipitation of the nickel with hydrogen sulphide, converting the nickel sulphide formed to nickel oxide, and weighing as such, an investigation of some recent methods was made, and their accuracy noted.

Dimethylglyoxime Method.

O. Brunck, in *Stahl und Eisen*, states that dimethylglyoxime, an organic compound, has proved a very efficient reagent for the determination of nickel in various substances, and with certain modifications can be used to determine nickel in iron and steel.

After conducting a number of experiments for the determination of nickel in steel with this reagent the following procedure was found to produce the best results:—

Weigh out 1 gm. of the nickel steel, place in a 250 cc. beaker, cover, add 20 cc. of hydrochloric acid (sp. gr. 1.12), heat gently till steel is dissolved, keeping beaker covered; oxidise with 6 to 7 cc. of nitric acid (sp. gr. 1.20). Continue heating a few minutes longer to complete the oxidation, add 20 grms. of tartaric acid dissolved in 20 cc. of water, remove from fire and cautiously add a strong solution of potassium hydroxide till solution is nearly neutral, a change of colour indicating this condition. Volume of solution should now be about 200 cc.

If solution is made alkaline, slightly acidify with acetic acid, heat to boiling, and add 15 to 20 cc. of a 1 per cent alcoholic solution of dimethylglyoxime with stirring.

Ammonia is then cautiously added until the solution smells slightly of it; while still hot filter on a weighed Gooch crucible, wash thoroughly with warm water, dry in oven at 110–120° C. for forty-five minutes, cool in desiccator, and weigh.

Nickel glyoxime is a red crystalline salt, contains no water of crystallisation, sublimes at 250° C., without decomposition, and contains 20.32 per cent nickel.

To test the accuracy of the method 0.2 gm. of chemically pure nickel ammonium sulphate and 1 gm. of common steel were weighed out and put through the above procedure, and the following results obtained, check analysis being run:—

	Nickel present.	Nickel found.	Error.
	Per cent.	Per cent.	Per cent.
Test No. 1 ..	2.972	2.970	- 0.002
Test No. 2 ..	2.972	2.981	+ 0.009
Average ..	2.972	2.975	+ 0.003

In both cases the Gooch crucible containing the nickel glyoxime was heated until constant weight was obtained.

The results show this to be a very accurate method. It is easy to operate, and can be readily completed in one and a-half hours. The only objection to the method is the cost of the reagent, which is at present 10 cents per gm.

A reduction of this price is in view. The oxime is readily recovered by mixing the nickel salt with water to a paste, warming with potassium cyanide, filtering hot, and precipitating the oxime at once with acetic acid.

Cyanide Method.

This is the method most used now in steel laboratories, having superseded the old sulphide method.

After reviewing the work of Chas. M. Johnson of

Pittsburg, and Geo. S. Jamieson of Yale, on this subject, the following scheme, which is essentially a combination of both writers' methods, was found to give good results:—

Weigh out 1 grm. of the nickel steel in a 150 cc. beaker, dissolve in 20 cc. of (1:1) hydrochloric acid. When action ceases, add 10 cc. of nitric acid (sp. gr. 1.20); reduce to volume of 15 cc. by boiling, keeping beaker covered, remove from fire, add 32 cc. of 25 per cent sulphuric acid in water. Transfer to a 400 cc. beaker, add 4 grms. of anhydrous sodium pyrophosphate, and 5 grms. of citric acid, stir well, and then slowly add ammonia till the precipitate just dissolves and the solution acquires a faint odour of ammonia.

If too much ammonia is added nearly neutralise by the careful addition of nitric acid; dilute to about 150 cc., cool to below 20° C., add 2 cc. of a 10 per cent solution of potassium iodide, and enough tenth-normal silver nitrate solution, the volume of which must be noted, to produce a distinct turbidity. Slowly run in the standardised potassium cyanide, stirring thoroughly till the turbidity just disappears, and the solution assumes a light golden yellow colour.

The solution should remain bright for five minutes, otherwise the titration is incomplete.

The end-point is best observed when the beaker is placed upon a white paper having an elliptical hole in it under which is placed a black glazed paper for contrast.

Make the proper deduction for silver nitrate in calculating results.

Standard Solution.

Prepare an exact tenth-normal silver nitrate solution, 1 cc. of which equals 0.002935 grm. of nickel.

Standardise the potassium cyanide against this solution by taking 20 cc. of cyanide in a 250 cc. beaker, diluting to 150 cc. with cold water, adding 2 cc. of a 10 per cent potassium iodide solution, running in silver nitrate until a distinct turbidity is produced, and then slowly adding the cyanide till the turbidity just disappears. From the amount of silver nitrate used the strength of the cyanide in terms of nickel is readily found.

The potassium cyanide should be made up approximately tenth-normal and 5 grms. of potassium hydroxide added per litre in order to improve its stability, frequent standardisations being necessary.

It is perhaps better to standardise the potassium cyanide against a steel of known nickel content, but the theoretical value used in the tests given below indicate very satisfactory results.

Two-tenths grm. of chemically pure nickel ammonium sulphate and 1 grm. of common steel were weighed out and put through the above procedure, and the following results obtained for six tests:—

	Nickel present. Per cent.	Nickel found. Per cent.	Error. Per cent.
Test No. 1 ..	2.97	3.00	0.03 +
Test No. 2 ..	2.97	2.99	0.02 +
Test No. 3 ..	2.97	2.99	0.02 +
Test No. 4 ..	2.97	3.00	0.03 +
Test No. 5 ..	2.97	2.98	0.01 +
Test No. 6 ..	2.97	2.99	0.02 +
Average ..	2.97	2.99	0.02 +

Check analyses by this method can be completed in fifty minutes.

Resumé.

The dimethylglyoxime is more accurate than the cyanide method, and should be employed in all umpire and check work where exact determinations are desired.

The cyanide is a good, quick, accurate method, particularly adapted to routine laboratory work. It is easy to conduct, though the operator should have some experience with the end-point, the greatest source of error in the method.—*The Chemical Engineer*, xiv., No. 1.

THE QUANTITATIVE DETERMINATION OF KETONES IN ESSENTIAL OILS.

By E. K. NELSON.

WHILE we have general methods for the estimation of alcohols, esters, phenols, and aldehydes in oils, such a method seems to be wanting in the case of ketones. Some substances of this class, as for example, camphor, do not react with sodium bisulphite. Others, while they may react with bisulphite, cannot be even approximately estimated by its use.

The methods of Sadtler (*Am. Journ. Pharm.*, pp. 76, 84; *Journ. Soc. Chem. Ind.*, xxiii., 303) and Labbé (*Bull. Soc. Chim.*, xxiii., 283), while valuable in many cases, could not be accepted as general methods because the reactions involved are not characteristic of all ketones.

All the ketones usually found in essential oils, however, do react with hydroxylamine to form oximes. The method of Walther (*Pharm. Centrbl.*, pp. 41, 613), depending upon the transformation of the ketone into oxime on boiling with a standard alcoholic solution of hydroxylamine hydrochloride in the presence of alkali, and the determination of the amount of the reagent thus consumed by titration of the excess on completion of the reaction, seemed to offer advantages as a general method for the analysis of ketone-bearing oils. Walther experimented on the estimation of citral and carvone, but does not speak of having tried the method on other ketones, or aldehydes. The following work was undertaken to test the accuracy of Walther's method on ketones in general. The ketones used were prepared from the oils in which they occur, or were obtained in some cases on the market and purified. In every case the method was carried out the same way. The standard hydroxylamine solution was prepared by dissolving 20 grms. hydroxylamine hydrochloride in 30 cc. water, and adding 125 cc. aldehyde-free alcohol. One to 2 grms. of the substance were boiled in a water-bath under a reflux with 35 cc. of this reagent, and 2 grms. sodium bicarbonate, cooled, 6 cc. HCl added, through the condenser, followed by water, and the mixture made up to 500 cc. The solution was filtered, and in an aliquot part of the filtrate the free acid was neutralised by running in N/2 NaOH, using methyl-orange. Phenolphthalein was then added, and the hydroxylamine left in excess of that required to form oxime was titrated with N/10 NaOH. The results in the following table were obtained.

Ketone or (aldehyde).	Wt. substance.	35 cc. reagent require N/10 NaOH.	Excess reagent require N/10 NaOH.	Time of boiling. Hrs.	Amount of substance required. Percent.
Carvone ..	2.3508	605.5	455.5	½	96.18
	2.3343	605.5	454.5	1	97.51
	2.2819	605.5	455.0	1	99.41
	1.9493	607.8	479.5	½	99.12
Pulegone ..	2.2852	605.5	452.5	½	101.77
	2.3228	605.5	451.5	1	100.77
	1.025	—	—	½	92.3
Camphor ..	1.0626	—	—	1	97.13
	2.0509	—	—	2	99.08
	1.7177	—	—	2	101.5
Thujone ..	2.2793	604.6	459.0	½	97.1
	2.2903	604.6	458.0	1	97.3
Menthone ..	2.1416	—	—	1	97.5
Fenchone ..	0.9026	578.2	527.3	2	85.7
	1.1823	578.2	540.6	1	50.6
Benzaldehyde ..	2.5447	606.7	375.0	½	96.5
	2.5278	606.7	376.0	1	96.7

Considering the nature of the work and the difficulty of preparing absolutely pure materials to start with, these results may be considered as fairly satisfactory except in the case of fenchone. As this is a rather rare ketone, however, and as it is present in but few oils and in those only in small amount, a method for its estimation is not so necessary.

In the case of spearmint oil the Walther method was tried in comparison with the estimation of the carvone by absorption in boiling sodium bisulphite solution as well as by the Labbé method.

Results on Carvone : Spearmint Oil.

Sample.	Labbé's method.	Walther method.	Absorption by boiling NaHSO ₃ .
1	54.7	58.4	55.0
		53.1	
2	61.3	65.5	67.5
		66.4	
3	—	61.43	61.5
		60.7	

A sample of tansy oil, assayed by the Walther method, gave thujone = 68.56 and 65.42 per cent. A sample of wormwood oil gave thujone = 33.15 per cent and 31.24 per cent. Pennyroyal oil gave 81.87 per cent ketone by this method calculated as C₁₀H₁₆O. A mixture of pulegone with at least two other ketones is present in pennyroyal oil. A sample of rosemary oil gave 30.33 and 30.24 per cent ketone calculated as camphor.

The Walther method cannot be recommended for the assay of any particular ketone-bearing oil until the influence on the reagent of other substances in the oil has been determined by working on known mixtures, and comparison, when that is possible, with other methods.

This work will require time. For the present it seems that the assay of oils in which carvone, camphor, pulegone, or thujone is the main constituent can be carried out with fair accuracy by this method, at least affording a criterion of the purity of such oils.—*Journal of Industrial and Engineering Chemistry*, iii., No. 8.

THE USE OF SODIUM PARATUNGSTATE IN THE DETERMINATION OF CARBON DIOXIDE IN CARBONATES AND NITROGEN PENTOXIDE IN NITRATES BY LOSS ON IGNITION.

By F. A. GOOCH and S. B. KUZIRIAN

FROM certain carbonates, like those of magnesium, zinc, and cadmium, carbon dioxide may be expelled by simple ignition at a moderate temperature, leaving an oxide in definite and weighable condition. In the case of calcium carbonate, this process of decomposition is completed only at the high heat of the blast-lamp, and the reaction, being easily reversible in the atmosphere containing carbon dioxide evolved in the ignition or produced in the source of heat, may leave the oxide not quite pure. Strontium carbonate and barium carbonate are not entirely broken up by simple ignition under the conditions ordinarily available in analysis; nor are the alkali carbonates. For the decomposition of refractory carbonates it is customary to make use of a suitable flux which, by combining with the oxide, will aid in the expulsion of the carbon dioxide. Anhydrous borax (Fresenius, *Zeit. Anal. Chem.*, i., 181), silicon dioxide (Rose, *Ann. Phys.*, cxvi., 635; Fresenius, *Zeit. Anal. Chem.*, i., 184; Richards and Archibald, *Proc. Am. Acad.*, xxxviii., 443), potassium dichromate (Rose, *Ann. Phys.*, cxvi., 131; Fresenius, *Zeit. Anal. Chem.*, i., 183), and, recently, sodium metaphosphate (Lutz and Tschischikoff, *Chem. Zentralblatt*, 1905, i., 564; Böttger, *Zeit. Anal. Chem.*, xlix., 487) have been thus used in the analysis of carbonates, and they are applicable similarly to the determination of nitrogen pentoxide in nitrates which leave definite oxides on ignition. Such fluxes, moreover, serve the very essential end of conserving the residual oxides in definite and stable form for weighing under the ordinary atmospheric condition of the balance room. Of those mentioned the first two, borax and silicon dioxide,

require prolonged ignition to bring them to constant weight before making use of them to react with the carbonate or nitrate; and generally they yield in the fusion process a pasty magma, so that prolonged heat at a high temperature is necessary to the complete expulsion of the gaseous product. Sodium metaphosphate, though more fluid in fusion, also demands prolonged care in the preparation. Potassium dichromate is too easily decomposed with loss of oxygen to be employed in exact processes demanding long continued fusion or heating to temperatures much above its fusing point.

These are points which have been sufficiently emphasised in the work to which reference has been made.

In sodium paratungstate of composition corresponding approximately to the formulæ 5Na₂O.12WO₃, or Na₁₀W₁₂O₄₁, we have material very easily prepared, stable in fusion, and well suited for use as a flux in the rapid determination of the loss of carbonates and nitrates on ignition. For the following experiments the sodium paratungstate was prepared by dehydrating and fusing over the blast-lamp a known weight of normal sodium tungstate, Na₂WO₄.2H₂O, adding an equal weight of tungsten trioxide, WO₃ (previously ignited with care to remove all ammonia and to insure complete oxidation), and heating to clear fusion. The cooled mass, which is very easily pulverised, was ground in a mortar, and bottled. From this material kept in a desiccator over sulphuric acid (though not more than ordinarily hygroscopic), portions were weighed for the analytical determinations. Approximately half the weight of the paratungstate is tungsten trioxide (molecular weight 232), and this should be capable of expelling carbon dioxide (molecular weight 44) to the amount of one-fifth its own weight, and of nitrogen pentoxide (molecular weight 108.02) to an amount one-half its own weight. The weights of paratungstate used were therefore always in excess of ten times the weight of carbon dioxide and four times the weight of nitrogen pentoxide to be expelled. In the following determinations it was the practice to weigh a platinum crucible, introduce the dried carbonate, and weigh again, add a suitable amount of the prepared sodium paratungstate, stir carefully with a platinum wire with care to avoid mechanical loss, and weigh again. The crucible was heated over a Bunsen burner, first at very low heat and then to fusion of the mixture for five minutes, cooled in a desiccator over sulphuric acid, weighed, and re-ignited to test the constancy of weight. The constant weight was usually got in the first ignition. In Table I. are given the results of the estimation of carbon dioxide in calcite.

TABLE I.—Analysis of Calcium Carbonate (Calcite).

CaCO ₃ taken (grm.).	Na ₁₀ W ₁₂ O ₄₁ taken (grms.).	Loss on ignition (grm.).	Theory for CO ₂ (grm.).	Error (grm.).
0.5000	2.5	0.2195	0.2198	-0.0003
0.5000	2.5	0.2206	0.2198	-0.0008
0.5000	2.5	0.2200	0.2198	-0.0002
0.5000	2.5	0.2203	0.2198	-0.0005
0.5000	2.5	0.2200	0.2198	-0.0002
0.5000	2.5	0.2204	0.2198	-0.0006
0.5000	2.5	0.2190	0.2198	-0.0002
0.5000	2.5	0.2200	0.2198	-0.0002

The strontium carbonate used in the experiments given below was prepared with great care. Strontium chloride, chemically pure, was partially precipitated by strong hydrochloric acid, washed with hydrochloric acid, dissolved in water, and added in dilute solution drop by drop from a stoppered funnel to a saturated solution of ammonium carbonate heated to the point of decomposition. The precipitated carbonate was carefully washed, dried, washed again with ammonium carbonate and then with boiling water, and dried below red heat. In Table II. are the results obtained with this preparation of strontium carbonate.

TABLE II.—Analysis of Specially Precipitated Strontium Carbonate.

SrCO ₃ taken (grm.).	Na ₂ WO ₄ taken, approx. (grms.).	Loss on igni- tion (grm.).	Theory for CO ₂ (grm.).	Error (grm.).
0.5000	2.5	0.1488	0.1490	-0.0002
0.5000	2.5	0.1494	0.1490	+0.0004
0.5000	2.5	0.1494	0.1490	+0.0004
0.5000	2.5	0.1490	0.1490	—
0.5000	2.5	0.1496	0.1490	+0.0006
0.5000	2.5	0.1486	0.1490	-0.0004

With barium carbonate prepared from the chloride by partial precipitation with strong hydrochloric acid, solution of the precipitated chloride in water, gradual addition of the solution with constant stirring to a hot solution of ammonium carbonate, careful washing, and drying, the results given in Table III. were obtained.

TABLE III.—Analysis of Specially Precipitated Barium Carbonates.

BaCO ₃ taken (grm.).	Na ₂ WO ₄ taken, approx. (grms.).	Loss on igni- tion (grm.).	Theory for CO ₂ (grm.).	Error (grm.).
0.5000	2.5	0.1120	0.1115	+0.0005
0.5000	2.5	0.1125	0.1115	+0.0010
0.5000	2.5	0.1109	0.1115	-0.0004
0.5000	2.5	0.1113	0.1115	-0.0002
0.5000	2.5	0.1123	0.1115	-0.0008

The similar use of sodium paratungstate for the determination of the nitrogen pentoxide in nitrates is shown in Table IV.

TABLE IV.—Analysis of Chemically Pure Nitrates of Commerce, after Drying.

Nitrate taken (grm.).	Na ₂ WO ₄ taken (grms.).	Loss on igni- tion (grm.).	Theory for Na ₂ O (grm.).	Error (grm.).
KNO ₃ —				
0.5000	1.5	0.2668	0.2670	-0.0002
0.5000	1.5	0.2678	0.2670	+0.0008
0.5000	1.5	0.2674	0.2670	+0.0004
0.5000	1.5	0.2672	0.2670	+0.0002
0.5000	1.5	0.2675	0.2670	+0.0005
Sr(NO ₃) ₂ —				
0.5000	2	0.2544	0.2543	+0.0001
0.5000	3	0.2546	0.2543	+0.0003
Ba(NO ₃) ₂ —				
0.5000	3	0.2073	0.2067	+0.0006
0.5000	3	0.2076	0.2067	+0.0009

From the results of the experiments described above it is obvious that sodium paratungstate, easily prepared and stable, makes an excellent flux for use in the rapid determination of carbon dioxide and of nitrogen pentoxide by loss on ignition. *American Journal of Science.*

THE ESTIMATION OF VERY SMALL AMOUNTS OF CALCIUM BY MEANS OF POTASSIUM PERMANGANATE.

By L. T. BOWSER.

THE well-marked difficulties attending the use of both the potassium oleate and the turbidity method for the determination of small amounts of calcium suggested the advisability of working out some procedure as simple as either of these but more accurate, as well as less subject to defects. At the time this matter claimed attention the writer had just completed a method for the estimation of potassium in very small amounts as the cobalti-nitrite, titrating the precipitate with very dilute potassium permanganate, and the idea occurred that a similar procedure might serve for the estimation of calcium. Preliminary trials showed that it was entirely feasible to do this, and a

careful investigation was made to determine the best conditions for accurate work. The results obtained and conclusions drawn may be of interest to others, hence will be briefly presented.

The method is essentially an extension of the well-known permanganate titration, so carried out as to be applicable in cases where calcium is reckoned only in parts per million. To the solution to be tested, of a volume of from 5 to 10 cc., a few drops of ammonium hydroxide are added, then about 0.4 grm. of powdered ammonium chloride. It is then heated to boiling and 0.2 grm. powdered ammonium oxalate added, the boiling being continued for a moment in order to make the precipitate as granular as possible. This boiling is best accomplished by setting the beaker, not over 50 cc. in capacity, on a wire gauze with Bunsen burner below. For the comfort of the analyst's hands it is well to use a circle of asbestos paper to cover the entire gauze save for a circle in the centre just large enough to admit the bottom of the beaker. After the completion of this boiling the solution in the beaker is diluted with approximately its own volume of 3 per cent ammonia to prevent crystallisation of ammonium oxalate, then allowed to stand for some time, preferably two or three hours if the best results are sought.

Filtration is carried out under suction, using a filter of the Shimer form with an asbestos pad about one-fourth of an inch in thickness. For such small amounts of precipitate as are involved a tube much smaller than that used in ordinary work is advisable. The one in use here is of one-half-inch internal diameter and 2 inches length, fitted with a small perforated aluminium plate. After the precipitate has been collected on the asbestos pad it is thoroughly washed with 3 per cent ammonia to free it from excess of ammonium oxalate. The wash liquid should preferably be hot, although practically as good results may be attained if it is cold. The pad is pushed out and placed in the precipitating beaker, then water enough added to thoroughly moisten the asbestos and give a few cc. in excess.

The precipitate is decomposed by 1 cc. of 1/1 sulphuric acid and titrated with N/200 KMnO₄, the excess of KMnO₄ being titrated back by means of N/200 oxalic acid. All titrations are carried out with the titrated solution kept at nearly the boiling-point. With a little practice the end-point of this reaction may be noted easily and with precision. From the results of the titration a blank, to be determined by a separate titration, must be deducted as an allowance for permanganate consumed by the asbestos, water, and sulphuric acid used. The first blank titration of a pad of asbestos oxidises out practically all the impurities, and a second one should be made for the real blank to be deducted. Practically all of the permanganate consumed is due to the 1 cc. of sulphuric acid, as ascertained by a number of trials, hence there is necessity for care that exactly the same amount be used every time. Almost every blank made by the writer has been 0.23 cc., although this figure would no doubt vary with the conditions. The same asbestos is used over and over again so long as it will make a good pad, and one blank serves for all. As many as twelve determinations have been made, using one portion of asbestos.

For some purposes sufficient accuracy may be attained by using for the titration an ordinary 50 cc. burette graduated to tenths of a cc., but for the most accurate work a small one graduated in fiftieths or hundredths is to be preferred, and this may, if desired, be read to two hundredths of a cc. There is in use here a 2 cc. size graduated in fiftieths for permanganate, and a 1 cc. graduated in hundredths for oxalic acid. Both are fitted with tips drawn out so fine that the drops are very small, a size such that ten drops of solution which equals 0.15 cc. is very satisfactory. A short rubber tube between the burette and small tip, with a glass bead in the tube to take the place of the more usual stopcock, gives a very delicate and satisfactory control of the rate of flow. The burettes are filled by inserting the tip in the desired solution and

drawing it up by suction, taking care to avoid contamination in any way. When these small burettes are used in titrating it is well to add the greater part of the permanganate by means of a 5- or 10-cc. pipette, then to complete the titration with the burette.

Potassium permanganate in such a dilute state does not oxidise as much as it should by theory, and it is necessary to standardise it against a calcium solution of known strength, under conditions similar as regards concentration and manipulation to those met in actual practice. Thus a N/200 solution such as used here should by theory oxidise 0.1002 mgrm. Ca per cc., whereas it is actually equal to only about 0.0793 mgrm. No satisfactory explanation of this behaviour can be made at this time, but the matter is being made the subject of a study from which interesting results seem probable. That the best possible results may be secured it is important that an amount of solution be taken, such that not less than 4 cc. of N/200 permanganate shall be required to oxidise the calcium present, preferably a somewhat larger volume, and the same precaution must be observed when standardising the permanganate. In case smaller amounts are used than those specified, there seems to be a tendency toward high results. It will be readily seen that this is a matter involving the total amount of calcium present rather than its initial concentration, and very good results may be obtained on exceedingly dilute solutions by taking a large volume and evaporating to the desired concentration. It is necessary to work with a final volume of 5—10 cc. of solution in order to overcome, to as great an extent as possible, the solvent effect of the water present.

By the use of this method extremely accurate and concordant results may be obtained in nearly every case, provided due care is exercised. The following results, taken at random from a large number secured in trying out the method, are typical of what may be expected. Table I. gives a series on which was based the standardisation of the permanganate solution.

TABLE I.

No.	Sol. used. Cc.	KMnO ₄ consumed. Cc.	Mgrm. Ca used.	Mgrm. Ca found.	Parts per million used.	Parts per million found.
1.	10	4.300	0.3429	0.3410	34.29	34.10
2.	10	4.335	0.3429	0.3438	34.29	34.38
3.	10	4.315	0.3429	0.3422	34.29	34.22
4.	10	4.340	0.3429	0.3442	34.29	34.42
5.	10	4.345	0.3429	0.3446	34.29	34.46
6.	10	4.310	0.3429	0.3418	34.29	34.18

Average 4.324

From the average amount of KMnO₄ used, 4.324 cc., we find that 1 cc. oxidises 0.0793 mgrm. Ca, and from this the recorded amounts are calculated. It will be noted that the agreement here is very close for a method involving such minute amounts. In Table II. is shown the results of a series where the initial concentration was less and the total amount of lime greater.

TABLE II.

No.	Sol. used. Cc.	KMnO ₄ consumed. Cc.	Mgrm. Ca used.	Mgrm. Ca found.	Parts per million used.	Parts per million found.
1.	50	5.75	0.4285	0.4560	8.57	9.12
2.	50	5.53	0.4285	0.4385	8.57	8.77
3.	50	5.82	0.4285	0.4615	8.57	9.23
4.	50	5.81	0.4285	0.4610	8.57	9.22
5.	50	5.71	0.4285	0.4530	8.57	9.06
6.	50	5.74	0.4285	0.4550	8.57	9.10
7.	50	5.59	0.4285	0.4430	8.57	8.86
8.	50	5.415	0.4285	0.4320	8.57	8.64
9.	50	5.425	0.4285	0.4300	8.57	8.60
10.	50	5.45	0.4285	0.4320	8.57	8.64

Average 5.624

The agreement is not so close here, although toward the last of the set, as experience was gained, there was a considerable improvement. However, as a whole this series is quite satisfactory. What happens when too small a total amount of calcium is taken may be seen in Table III., the first five portions containing half the amount of the last six, and falling below the limit of 4 cc. of permanganate needed, equivalent to about 0.3 mgrm.

TABLE III.

No.	Sol. used. Cc.	KMnO ₄ consumed. Cc.	Mgrm. Ca used.	Mgrm. Ca found.	Parts per million used.	Parts per million found.
1.	50	3.34	0.2142	0.2650	4.29	5.30
2.	50	3.28	0.2142	0.2600	4.29	5.20
3.	50	3.40	0.2142	0.2695	4.29	5.39
4.	50	3.31	0.2142	0.2625	4.29	5.25
5.	50	3.27	0.2142	0.2595	4.29	5.19
Average					4.29	5.27
6.	100	5.31	0.4285	0.4210	4.29	4.21
7.	100	5.49	0.4285	0.4360	4.29	4.36
8.	100	5.46	0.4285	0.4330	4.29	4.33
9.	100	5.44	0.4285	0.4320	4.29	4.32
10.	100	5.45	0.4285	0.4330	4.29	4.33
11.	100	5.44	0.4285	0.4320	4.29	4.32

Average 4.32

This series is sufficient to satisfactorily illustrate the point that not less than 0.3 mgrm. of Ca should be present. This is the minimum limit, while there is apparently no maximum one. The last six results must be conceded to be exceedingly satisfactory, and constitute, along with those previously given, a very fair test of the capabilities of the method. It possesses a number of decided advantages over the other two, such as accuracy, speed, easy manipulation, and the absence of any necessity for preliminary decolorising of a solution to be operated upon. The procedure outlined is in a measure adapted from the turbidity method used by the Bureau of Soils (*Bull.* xxxi., 53), and prevents the danger of interference of magnesium. Uniformly good results have been secured by the method, and it is believed that its evident merits will commend it to those having occasion to estimate unusually small quantities of calcium for any purpose.—*Journal of Industrial and Engineering Chemistry*, iii., No. 2.

CORRESPONDENCE.

USE OF ACETYLENE IN LABORATORIES.

To the Editor of the Chemical News.

SIR,—I have been using acetylene gas for all analytical and experimental work for the last six years in a Government factory in Bengal, India, as no town gas is available there.

I have never had occasion to be troubled by any of the difficulties mentioned in the *CHEMICAL NEWS*, August 11th, 1911 (vol. civ., p. 72).

The difficulty (1) is nothing but low pressure. This will probably be removed by increasing the pressure of gas. My crucibles are always clean during incineration of the precipitates.

Burner-chimneys should be cleaned inside every morning by means of a brush, and the jet-hole wired through for easy passage of gas.

The difficulty (2): I have always used Thorn and Hoddles' "Curaze" purifier—which has been found to work admirably by absorbing all obnoxious gases. I always suspend crucibles on platinum wire loops over Bunsens. The platinum crucibles have never been so frosty as described.

but bottom outside has required polishing after every 50 to 60 fusions, and ignitions and platinum loops have required repair after 300 ignitions. The platinum apparatus had fared no better when I worked with coal-gas.

The generator in use is Thorn and Hoddle Patent 4.B.—I am, &c.,

HARI JUDA BHATTACHANGY, M.A.

Dakinsore, Calcutta, India,
September, 6, 1911.

REDUCTION OF SILVER CHLORIDE.

To the Editor of the Chemical News.

SIR,—In the Correspondence column of the CHEMICAL NEWS dated June 16th, 1911 (vol. ciii., p. 288) there is a process given by Edgar Booth for the reduction of silver chloride. In the fourth paragraph of the letter we have:—"When action had apparently ceased the mixture was boiled, diluted, and filtered. The silver formed by this method also dissolved completely in dilute nitric acid, being free from all traces of the chloride."

I had some silver residues in my laboratory which I took up to work for silver by the above process. I followed all the directions of the writer of the article. After the addition of the solution of Na_2O_2 the mixture was boiled, diluted, and filtered, but what I got in the filter-paper was not metallic silver, but blackish silver oxide, or more correctly brown silver oxide. I tried the same reactions twice, and I got the same brown precipitate on both occasions. What I want to know is whether the writer intended to say that metallic silver can be had by his process. If so, I believe there are some other conditions which the writer perhaps has left out.

The precipitate that I obtained was soluble in dilute nitric acid. In the filtrate (after the precipitate was separated) no trace of silver was found as Mr. Booth writes. Will you please publish this statement of mine and help me in solving my difficulty. I need not, I hope, repeat that I did not, by Mr. Booth's process, obtain metallic silver on either of the occasions on which I carried on my experiments.—I am, &c.,

N. N. GODBOLE, M.A., B.Sc.

D. J. Sind College Laboratory,
Karachi, India,
September 6, 1911.

CURIOUS THERMAL PHENOMENON.

To the Editor of the Chemical News.

SIR,—I note in the communication of Mr. E. G. Bryant, August 25th (CHEMICAL NEWS, vol. civ., p. 96), he speaks of a failure in his experiment when he used an iron bar bent at right angles and heated. It seems quite possible that the bending of the bar interfered with the phenomenon. I have frequently noticed that an iron rod bent cold conducts heat more slowly along the bend than if it is straight. One or two mechanics with whom I have spoken on the subject have talked of the phenomenon as one familiar to them individually. I cannot say how generally it is known, but have seen no statement about it in the literature. The somewhat indefinite explanation was given me that it was due to the tension of the fibres of the iron.—I am, &c.,

ELWYN WALLER.

7, Franklin Place, Morristown, N.J.,
September 18, 1911.

Syntheses of β -Substituted Diketones, Ketonic, Ether Salts, and Enolic Ethers by means of Sodium Ketones.—A. Haller and Ed. Bauer.—Acid chlorides, especially benzoyl chloride, react with the sodium derivatives of ketones to give a mixture of substituted diketones and isomeric enolic ethers. In presence of some sodium ketones, β -iodopropionic ether reacts like an alcoholic iodide, and gives δ -ketones.—*Comptes Rendus*, cxiii., No. 3.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

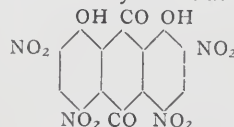
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clii., No. 2, July 10, 1911.

Extraction of Gases from Copper Heated in Vacuo.—Marcel Guichard.—When copper is heated in vacuo gas is always evolved, but it is difficult to eliminate all the occluded gases by the action of heat. It is always necessary to continue heating for many hours, and to let the surface of the metal be as large as possible. At 630° a copper wire of surface 1.95 sq. cm. per 100 grms. liberated 8.5 cc. of gas in seven hours, and continued heating led to the evolution of further small quantities.

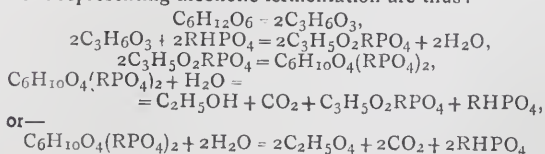
Lactonisation of α -Ketonic Esters.—H. Gault.—The esters of α -ketomonacids and of α -ketodiacids very readily undergo lactonisation under the influence of various condensation agents, a molecule of alcohol being eliminated from 2 molecules of the ketonic ester. Thus sodium ethylate, sulphuric acid, hydrochloric acid, and amines very readily lactonise α -ketoglutaric ester, α -ketosuccinic ester and pyruvic ester giving keto-lactone carbonic esters, which are usually viscous liquids possessing the characteristic properties of acids. They give the reactions of enolic hydroxyl, colouring iron perchloride violet-red, reducing ammoniacal silver nitrate, and giving acylated derivatives.

Preparation of some Asymmetric Benzylalkyl-acetic Acids.—Ph. Dumesnil.—Methylethylacetophenone can be prepared by the action of sodamide on ethylphenylketone, and may be converted into methylethylbenzylacetophenone by heating with sodamide and benzyl chloride. From the ketone the corresponding amide may readily be obtained and converted into methylethylbenzylacetic acid by means of nitrous acid. Ethylpropylbenzylacetic acid can be prepared by similar reactions.

Constitution of Nitro Derivatives obtained by the Action of Nitric Acids on Aloins.—E. Léger.—When nitric acid acts on nitrated aloha-modin chrysammic acid is formed as well as trinitro-*m*-oxybenzoic acid. A larger yield of the latter may be obtained by the action of nitric acid on chrysammic acid, and hence it may be deduced that the real generator of the oxybenzoic acid is the chrysammic acid. The formation may be due to the rupture of the anthraquinone nucleus subsequent to hydration, and the formula of chrysammic acid must be—



Mechanism of Alcoholic Fermentation.—Alexandre Lebedeff.—Up to a concentration of 5 per cent dioxoacetone ferments as well as saccharose; above 5 per cent only one-half is transformed. All fermentable sugars give the same phosphoric acid ester with phosphoric acid at the commencement of fermentation, viz., $\text{C}_6\text{H}_{10}\text{O}_4(\text{H}_2\text{PO}_4)_2$. This may be explained by assuming that the hexose is first decomposed to triose, which combines with the phosphoric acid, giving an ether, $\text{C}_3\text{H}_5\text{O}_2\text{H}_2\text{PO}_4$, and this immediately condenses to $\text{C}_6\text{H}_{10}\text{O}_4(\text{H}_2\text{PO}_4)_2$, and then undergoes hydrolysis, giving alcohol and carbon dioxide. The equations representing alcoholic fermentation are thus:—



Dimethylidipentene, produced by Combustion of Dimethylcaoutchouc.—A. H. Richard. —Methylisoprene behaves on polymerisation exactly like isoprene. Under the influence of light or heat it gives a mass like caoutchouc, which, on dry distillation, yields as the chief product a homoterpene.

Vol. cxliii., No. 3, July 17, 1911.

New Methods of preparing Benzylamines and Hexahydrobenzylamine.—Paul Sabatier and A. Mailhe. —Benzylamines can readily be prepared by the action of ammonia on benzyl alcohol in presence of thoria. At 330° primary benzylamine is the principal product, and at 370–380° dibenzylamine. Benzylamine can be hydrogenated over nickel at 170–180°, giving hexahydrobenzylamine, which is a colourless hygroscopic liquid. It yields a crystalline carbonate with the carbon dioxide of the air, and phenyl benzyl urea with phenyl isocyanate.

Coefficients of Magnetisation of Gold.—M. Hanriot and F. Raoult. —When an alloy of gold and silver is treated with nitric acid a spongy mass of "brown-gold" is obtained; it appears to consist of a mixture of varying proportions of ordinary or α gold and a new β -modification. Both varieties are diamagnetic, but brown-gold always gives lower values than α gold.

Action of Oxidising Agents on Isopyromucic Acid.—G. Chavanne. —Hydrogen peroxide in alkaline solution splits the molecule of isopyromucic acid, giving maleic acid, CO₂, and a little formic acid. The oxidising action of bromine and water on isopyromucic acid also transforms it into maleic derivatives.

Transformation of Substituted Paraconic Acids into Isomeric Cyclopropane-dicarboxylic Acids.—Ph. Barbier and R. Locquin. —Certain lactonic acids can easily be transformed into the isomeric dibasic acids derived from cyclopropane by dissolving the dry acid in benzene, and allowing thionyl chloride to act on the solution at the temperature of the water-bath for twelve hours. Thus, phenylparaconic acid is converted into phenylcyclopropane-dicarboxylic acid. Probably the reaction takes place in two stages; in the first the lactonic chain opens and SOCl₂ is fixed, and in the second SO₂ and HCl are given off, and the chain closes again.

Bulletin de la Société Chimique de France.

Vol. ix.-x., No. 13, 1911.

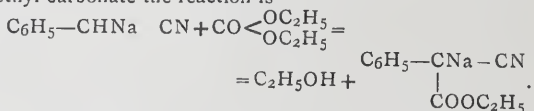
Influence of Dissolved Salts on the Partition of a Substance between Two Solvents.—Nicolas de Kolossofsky. —The author has studied the effect of dissolved salts upon the coefficient of partition of acetic acid between water and ether. The same quantity of salt diminishes the coefficient more the greater the concentration of the acid. When the concentration of the acid is kept constant the lowering of the coefficient increases with the amount of dissolved salt, and as long as the variations of the coefficient are relatively small they are proportional to the weight of the dissolved salt.

Preparation of Semi-permeable Membranes.—E. Fouard. —In this paper the author describes a new way of preparing semi-permeable membranes, which is an improvement upon that of Traube and Pfeffer, and also a differential method of measuring osmotic pressures, by means of which it is possible to arrive at the correct values of molecular weights. This is specially applicable to the determination of very high molecular weights.

Action of Sulphuryl Chloride on Metals.—H. B. North. —Two grms. of finely powdered metal and an excess of sulphuryl chloride were sealed in a glass tube, and left at the ordinary temperature for some hours. If no reaction took place the temperature was raised to 150°, and then, if necessary to 300°. Above 300° an explosion usually took place. In the case of gold the trichloride was formed, 2Au + 3SO₂Cl₂ = 2AuCl₃ + 3SO₂. With platinum the reaction was Pt + 2SO₂Cl₂ = PtCl₄ + 2SO₂. Silver, zinc, cadmium, and iron were not attacked, even at 300°.

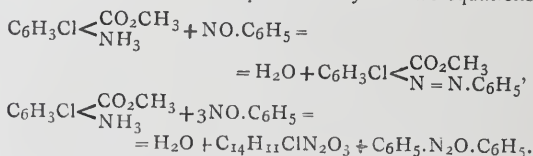
Colorimetric Determination of Phosphoric Acid.—I. Pouget and D. Chouchak. —A nitric acid solution of the substance in which the P₂O₅ is to be determined is evaporated to dryness, the residue is taken up with nitric acid, the liquid is decanted off, and strychnine nitromolybdate solution is added. The solution for comparison is made by adding 10 cc. of 35 per cent nitric acid to 3 cc. of a solution of phosphoric acid containing 10 mgrms. P₂O₅ per litre, making up to 47 cc. with water, adding 2 cc. of a solution of strychnine nitromolybdate, and finally making up to 50 cc. The strychnine solution may be prepared by mixing 10 cc. of a 15 per cent solution of sodium molybdate, 2.5 cc. of pure nitric acid, and 1 cc. of a saturated solution of strychnine sulphate.

Action of Ether Salts on Monosodium Benzyl Cyanide.—F. Bodroux. —In presence of ether ethyl benzoate combines energetically with monosodium benzyl cyanide, yielding 1,2-diphenyl-1-propanone-3-nitrile. With ethyl carbonate the reaction is —



Ethyl oxalate undergoes a similar condensation, the product being ethyl phenylcyanopropylate, while with ethyl succinate the product is 2,7-diphenyl-octave-3,6-dione-1,8-dinitrile.

Preparation of Ortho-substituted Azoic Acids.—P. Freundler. —The ortho-substituted azoic acids can be prepared by the condensation of nitrosobenzene with the *o*-aminobenzoic ethers. In the case of chloranthranilic ether the reaction can be represented by the two equations



Small quantities of the substituted azoic acids can also be obtained by the condensation of amines with *o*-nitrosobenzoic acid.

Composition of Oil-seeds from French West Africa.—A. Hebert. —In this paper the author publishes the results of the analysis of many oil-seeds, obtained in the forests of the Ivory Coast. He gives the total percentages of fats and their physical constants, and the percentages of fatty acids.

MISCELLANEOUS.

Literary Intelligence.—Messrs. J. and A. Churchill have just ready for publication Volume V. of the new edition of Allen's "Commercial Organic Analysis." This volume has been re-written under the editorship of Mr. W. A. Davis, B.Sc., and Mr. S. S. Sadtler, S.B. The subjects and authors are as follows:—Tannins, Leather, Dyes, and Colouring Matters (Classes one to five), by W. P. Dreaper; Diphenylmethane and Triphenylmethane Colouring Matters, &c., by J. T. Hewitt; Colouring Matters of Natural Origin, by W. M. Gardner; Analysis of Colouring Matters, by W. P. Dreaper and E. Feilmann; Inks, Carbon Papers, Typewriter Ribbons, &c., by P. H. Walker; Colouring Matters in Food, by A. F. Seeker. It will be seen that each subject is dealt with by an expert in his department.

NOTES AND QUERIES.

Softening Water.—Can any reader give me any information concerning the "Permutit" system of treating very hard water, and where there is a plant in this country in full working order.—R. W. V.

THE CHEMICAL NEWS.

VOL. CIV., No. 2707.

ACTION OF NITON (RADIUM EMANATION) ON THE SALTS OF THORIUM.

By Sir WILLIAM RAMSAY.

I AM glad that other people have studied the action of niton upon solutions of salts, but I cannot help regretting that M. Herschfinkel did not consult me before performing the experiments which he described in the *Comptes Rendus* of July 24th (CHEMICAL NEWS, civ., 163).

In the first place, the 270 grms. of thorium nitrate were never exposed to the action of radium emanation. The aim of my experiments was to detect the helium produced by the salts of thorium, and after the lapse of more than six months I thought I could recognise the spectrum of helium in the gases which escape from the solution of thorium nitrate. I repeated the experiments four times with the same solution, and I never failed to observe (and to measure) a fairly large quantity of carbon dioxide which escaped from the solution.

The only remarkable thing was that each time the quantity of carbon dioxide seemed to be proportional to the time the solution had stood. It did not seem to me to be absolutely impossible that the thorium could decompose into carbon, which was oxidised to carbon dioxide.

To settle the question I freed a specimen of thorium nitrate from organic impurities, firstly, by heating to redness and then by dissolving in nitric acid. There is very little likelihood of the nitrate thus obtained containing carbon.

This solution was crystallised several times, the greatest possible precautions being taken to exclude dust, and some cubic centimetres of a solution of fine crystals of the nitrate were introduced into a little glass bulb.

This solution of the nitrate was exposed to the niton coming from 0.6 gm. of radium bromide, previously freed from carbon dioxide by contact for several hours with a piece of damp caustic potash, without being allowed to touch either grease or indiarubber. Mr. Aster and I always found carbon dioxide in the gases in the bulb. The nitrates of bismuth, mercury, and silver gave no trace of it.

In my opinion M. Herschfinkel's experiments prove only one thing, viz., that the specimen of thorium which he used contained compounds which yielded carbon dioxide after treatment with permanganate, which, moreover, itself usually gives a fairly large quantity of carbon dioxide when heated.—*Comptes Rendus*, cliii., 373.

SOME CONDITIONS AFFECTING CHEMICAL CHANGE.

THE energy contained in an atom operates in two forms, namely, atomic motion, and atomic attraction or affinity. Therefore for all practical and theoretical purposes an atom may be regarded as having two kinds of energy. For the immediate purposes of this paper the relative quantities of these energies present in any atom, or the amount by which one exceeds the other, is of no consequence. At this stage the points to be discussed do not require quantitative treatment. The factors affecting the question to be dealt with are not dependent upon by how much energy of motion exceeds energy of attraction and *vice versa*, but only upon the existence of any such excess. In other words, chemical affinity, or the ability of two

atoms to enter into stable combination, depends upon the existence of an excess of energy of attraction over energy of motion, always provided other conditions allow impact to take place between the atoms. On the other hand, if energy of motion is in excess of energy of attraction, although an impact takes place, combination between the atoms cannot result. The condition determining the occurrence of an impact is the direction in which the atoms are travelling relative to one another. Atoms capable of meeting must be moving in the same directions. Atoms moving in opposite directions will exercise mutual repulsion. It may be supposed that the path of an atom in motion is curved. Suppose two such paths have some point in common; then two atoms arriving at this point from opposite directions will be mutually repelled, whilst two atoms arriving there from the same direction may exercise mutual attraction. It is obviously only in the latter case that combination can result, and that only provided energy of attraction exceeds energy of motion.

The following diagram partly illustrates this. In the diagram of forces represented by Fig. 1, AA' represent energy of attraction, and are supposed to be equivalent to forces acting in the directions o and p respectively, and having

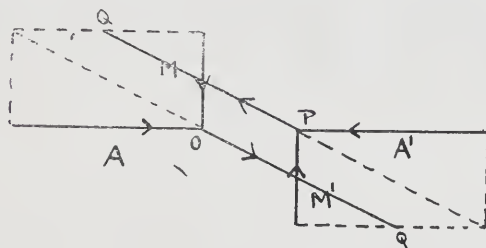


FIG. 1.

values twice as great as the forces MM' , which represent the energy of motion of the atoms at o and p . The distance OP is taken to represent the relative positions of the atoms when they first mutually enter their spheres of attraction. The same distance is taken to represent a unit of force in the diagram. The forces MM' are acting in the directions o and p respectively, and represent two atoms approaching each other from opposite directions.

The resultant forces, PQ and OQ , act in parallel but opposite directions, and being greater than the forces A and A' , will carry the atoms outside their spheres of attraction. Their motion after this is not within the question.

If the forces AA' and MM' are equal, the resultants PQ and OQ will still be parallel. Further, if MM' are greater than AA' , PQ and OQ will still be parallel. And if A equals M , whilst A' equals M' , but A is greater than A' by the proportion x , and M is greater than M' by the same proportion, then PQ and OQ will still be parallel.

Under any other conditions, provided the atoms are travelling in opposite directions, PQ and OQ will be divergent.

Fig. 2 shows one case. It can be seen from the resultants that repulsion has taken place. Fig. 3 is another example.

Therefore, since atoms travelling towards a common point from opposite directions are not likely to suffer actual encounter, the case of those approaching a given point from the same direction is the only one in which actual encounter can take place.

By constructing diagrams of forces in the way already adopted, it can be clearly shown that in those cases only where the sum of A and A' is greater than the sum of M and M' can stable union result, always given that the atoms are approaching their point of contact from the same direction. An encounter under the specified condition may take place, but if the energies of motion are together greater than the energies of attraction, the

resultants in the force diagram will be equal to an amount of energy sufficient to remove each atom out of the sphere of attraction of the other. In other words, a considerable rebound will be experienced by both.

From this various things are apparent. In the first place, although two atoms may have equal attraction one for the other, they may be travelling at speeds which prohibit chemical union. In other words, the rate at which they travel determines their power to unite. Thus, at a temperature of 3000° C. oxygen and hydrogen probably cease to combine, because the energy supplied to

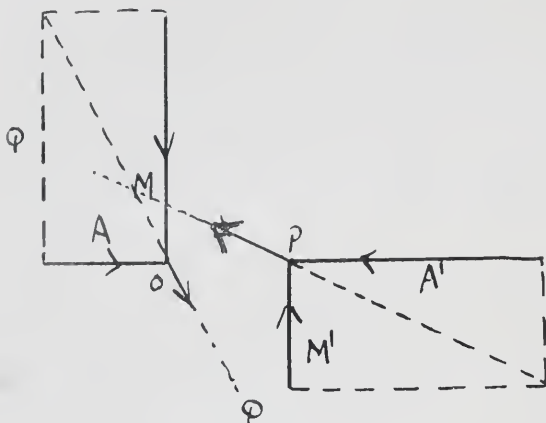


FIG. 2.

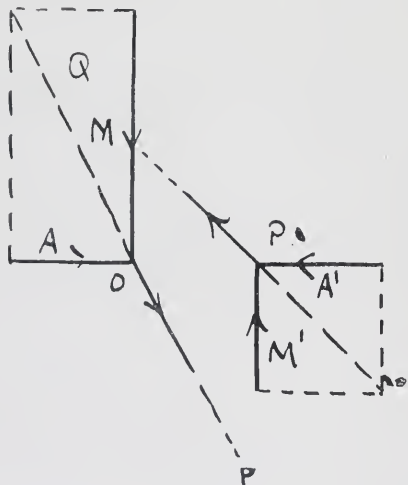


FIG. 3.

them at this elevated temperature is sufficient to make their speeds of atomic motion exceed their total attraction when both these are considered as forms of energy.

The heat of formation of a body must give us some indication of the amount of energy being used in the form of motion of the atoms or molecules of the reacting constituents. When hydrogen and chlorine unite to form hydrogen chloride gas 22000 calories are liberated. Each atom of a molecule of hydrogen or chlorine must be in motion within the molecule; that is, each molecule has locked within it a certain amount of energy of atomic motion, besides its molecular energy of motion. Now the energy of motion of a molecule must be related in some way to the energy of motion of the constituent atoms. In other words, the energy of motion of a molecule is the

resultant of the combined energies of motion of its constituent atoms and their combined absolute affinities. Thus, if the atomic affinities are high relatively to the energies of motion, the rate of travel, or the tendency for it, will be low, and *vice versa*. In speaking of the rate of travel of a molecule it must not be forgotten that the term is used in a strictly comparative sense; the rate of travel is low or high compared with the affinity strength. It may be in any case exceedingly great compared with time and distance. Now, when two atoms unite to form a molecule, the resultant is less than the sum of the forces operating, which points to a loss of energy, manifested in the heat of formation of the molecule. From the fact that hydrogen and chlorine unite to form hydrogen chloride, it appears that there is a certain amount of active molecular affinity above that required to lend stability to the individual molecules. It seems that the loss of energy is experienced by the energy of motion rather than the energy of attraction. In order to obtain nascent hydrogen or chlorine, in accordance with the reaction $H_2 + Cl_2 = 2HCl$, an amount of energy equal to that lost when the atoms combined to form molecules of hydrogen and chlorine must be absorbed. This energy is readily imparted in the form of heat, or, more slowly, light. It might be supposed that under ordinary circumstances of temperature and pressure, the molecules of hydrogen and chlorine are held together in a loose way by their molecular affinities, but not so as to form hydrogen chloride, the molecules themselves being still intact. A strain would arise in this way inside the molecules, but it would be quite small, since the tendency to break down into individual molecules, arising from the speed at which the molecules are moving, would be comparatively great. Therefore the degree of this aggregation is reduced to the minimum, and is little more than mere molecular collision, so that practically the whole of the energy needed to cause disruption of the molecule would be drawn from the heat supplied. Thus the heat absorbed to form nascent hydrogen and chlorine plus the heat of formation of hydrogen chloride represents the energy of motion of the hydrogen and chlorine atoms, *minus* the energy of motion retained within the molecule of hydrogen chloride. From consideration of this it seems possible to obtain figures representing the energy of motion of the atom of hydrogen or chlorine; and further, to obtain also a value for the absolute affinity of these elements expressed as energy.

The kind of motion taking place within a molecule is difficult to decide. The atoms are probably revolving about a point, synonymous with the centre of gravity of the molecule, which may be equidistant between each atom or otherwise, according to the circumstances of motion, attraction, and mass of the constituent atoms.

Bodies which break down with explosive violence on the application of small amounts of energy owe this property to the fact that their atoms possess a relatively high rate of motion within the molecule, so that only a small application of extra energy must upset the equilibrium. The energy developed by the explosion is the kinetic energy developed by the expansion of the products of explosion.

The catalytic action of water receives one possible explanation, considered in the light of the foregoing remarks. It is this; the water introduced will exist at ordinary temperatures as small molecular complexes, which may be capable of holding in solution a few molecules of the reacting bodies. The molecular motion of any body in a fairly dense medium such as water must be considerably less than when in a condition of freedom; it will be even still less when the molecules are held by a small congeries of water molecules, or, which is the same, when the concentration is great. Molecular combination, such as takes place between NH_3 and HCl in the presence of minute traces of moisture, then becomes possible. The same explanation may be applied in most instances of this nature, but the fact that dry NH_4Cl does not dissociate as usual at 350° C. is not so readily explained. In the first place,

it is clear that water, or a body exerting the same influence that water is supposed to exert, is necessary, and is the cause of dissociation. In this case, since the temperature, 350°C ., is apparently too high to allow the existence of water complexes, the solution of NH_4Cl is out of the question, and in this respect the solution theory advanced above is not affected by the case of NH_4Cl . The point that is evident is this, namely, the temperature of 350°C . does not give rise to sufficient increase of internal motion in the NH_4Cl molecule to cause instability, which is only brought about in the presence of individual water molecules. The formation of a hydrate of NH_4Cl which might affect its dissociability is out of the question at 350°C . The fact that combination, and also apparently solution, cannot take place at 350°C . seems to negative the possible influence of water as an electrolyte. Impact between molecules of water and NH_4Cl is also an unsatisfactory explanation, because if the impact were strong enough to cause breaking down of the molecule there is no reason why it should take place so as to form NH_3 and HCl in preference to any other possible division. The only assumption which appears legitimate is that water is not entirely divided into individual molecules at 350°C . If this is so, and small groups, invisible and fairly strongly united, do exist at 350°C ., it is possible for solution to proceed to a limited extent. In any case, it may be assumed that the NH_4Cl molecule becomes entangled with a group of water molecules, and is carried along by them at an accelerated speed. It may be assumed that the strain set up within the NH_4Cl molecule through this acceleration is sufficient to cause disruption with formation of NH_3 and HCl . In other words, the kinetic energy developed through the entanglement and subsequent breaking away of the NH_4Cl molecule is sufficient to impart an amount of energy of motion to its constituents great enough to cause instability, with consequent dissociation into NH_3 and HCl .

Residual affinity, according to the foregoing, is obviously no more than a part of the normal affinity of some preponderating atom or group. It will be able to operate with effect only if, together with the affinity of the other reacting body, it is greater than the sum of the energies of motion. It is in every way identical with normal affinity, and any distinction is artificial.

Facts bearing out the foregoing are the following:—

In no case does cooling cause decomposition; stability probably increases with decrease of temperature, because many changes can only take place and the resulting compounds only exist at low temperatures. On the other hand, elevation of temperature beyond that required for the initiation of chemical action often proves detrimental, causing decomposition, and at very high temperatures combination apparently ceases. Further, changes in pressure are observed to have much the same effect as changes in temperature.

Hence stability depends directly upon speed of atomic or molecular motion. Speed of atomic motion is directly proportional to rise or fall of temperature and is the primary factor in the determination of chemical change, after the direction of atomic movements has been considered.

Thus valency, the ratio of the combining powers of different elements or groups, may vary within reasonable limits, whilst absolute affinity remains constant for the same element under any conditions.

W.A.B.W.

September 22, 1911.

Character of Zymase.—A. Lebedeff.—The author's experiments prove that zymase is a typical diastase. The quantity of sugar fermented is nearly proportional to the quantity of co-enzyme, if the concentration of the latter is at least 20 per cent for active sugars.—*Bull. Soc. Chim.*, ix., x., No. 13.

NEW RARE EARTH COMPOUNDS.

By L. A. PRATT and C. JAMES.

THE salts given in this paper were prepared while searching for some crystalline compounds which might be useful for fractional crystallisation of the yttria earths.

Yttrium Methyl Sulphonate, $\text{Y}(\text{CH}_3\text{SO}_2\text{O})_3 \cdot 4\text{H}_2\text{O}$.

In the preparation of this salt, yttrium oxide was dissolved in methyl sulphonic acid and the solution evaporated. The residue was taken up in alcohol and precipitated by ether. The compound separated as a viscous mass, which rapidly became crystalline. It was separated from the liquid as far as possible with suction, and air dried. The salt was too soluble to be of value for fractional crystallisation.

Analysis.

Calculated ..	Y = 19.93	S = 21.54
Found	Y = 19.72	S = 21.42

Yttrium Methene Disulphonate, $\text{Y}_2(\text{CH}_2(\text{SO}_2\text{O})_2)_3 + 2\frac{1}{2}\text{H}_2\text{O}$?

This compound was prepared by dissolving yttrium oxide in methene disulphonic acid. The solution was evaporated, and treated with absolute alcohol and ether. The resulting precipitate was filtered, washed with ether, and air dried. The salt is very soluble.

Analysis.

Calculated	Y = 23.87
Found	Y = 23.76

Yttrium Methine Trisulphonate, $\text{YCH}(\text{SO}_2\text{O})_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$.

This salt was made by dissolving yttrium oxide in methine trisulphonic acid and evaporating the solution. Upon the addition of alcohol to this liquid the compound was completely precipitated. It was washed with alcohol on the suction and air dried. The salt is insoluble in alcohol, acetic acid, and only slightly soluble in nitric acid.

Analysis.

Calculated ..	Y = 21.96	S = 23.73
Found	Y = 21.91	S = 24.04

The methine trisulphonic acid for this compound was prepared by treating powdered acetanilide with fuming sulphuric acid (*Journ. Chem. Soc.*, lxxv., 280).

Yttrium Ethyl Sulphonate, $\text{Y}(\text{C}_2\text{H}_5\text{SO}_2\text{O})_3 \cdot 4\text{H}_2\text{O}$.

Yttrium oxide was dissolved in ethyl sulphonic acid, and the solution evaporated. The residue was taken up in alcohol, and upon treatment with ether the compound came down in a crystalline form. This was washed on a filter with ether and dried in the air. Like most of the other sulphonates this compound was very soluble.

Analysis.

Calculated	Y = 18.23
Found	Y = 18.05

Yttrium Camphor Sulphonate, $\text{Y}(\text{C}_{10}\text{H}_{15}\text{OSO}_2\text{O})_3 \cdot 7\text{H}_2\text{O}$.

In order to prepare this salt yttrium oxide was treated with camphor-sulphonic acid, and the resulting solution evaporated. The residue was taken up with alcohol and precipitated by ether. The compound came down in a crystalline form, and was filtered off and air dried. This substance was found to be very soluble.

Analysis.

Calculated	Y = 9.80
Found	Y = 9.82

Yttrium Oxymethyl Sulphonate.

In an attempt to make yttrium oxymethyl sulphonate, yttrium oxide was dissolved in oxymethyl sulphonic acid

and the solution evaporated on the water-bath. The residue was dissolved in alcohol and treated with an excess of ether. A sticky mass was thrown out, which failed to crystallise under any conditions.

Yttrium Salicylate, $Y[C_6H_4(OH)COO]_3 \cdot 3\frac{1}{2}H_2O$.

Since this salt is insoluble in water, it was advantageous in preparing it to first make the yttrium oxide into the formate, and to add to this the required amount of salicylic acid. This mass was boiled until all formic acid was volatilised. The precipitate was then filtered, washed with hot water, and dried in the air. The compound was crystalline and very insoluble.

Analysis.

Calculated		Y = 15.81
Found		Y = 15.73

Yttrium Phthalate, $Y_2[C_6H_4(COO)_2]_3 \cdot 3H_2O$.

To prepare this compound a known amount of yttrium oxide was dissolved in formic acid, and the required amount of phthalic acid added. The resulting mass was boiled to expel all formic acid. The liquid was then decanted off, and the residue boiled for some time with water. It was filtered, further washed with water, and dried in the air. The compound was very insoluble.

Analysis.

Calculated	Y = 24.58	C = 39.77	H = 2.50
Found ..	Y = 24.55	C = 39.48	H = 2.46

Yttrium Glycolate, $Y(CH_2OHCOO)_3 \cdot 2H_2O$.

This compound was prepared by dissolving yttrium hydroxide in glycolic acid and heating, when the compound separated out. The precipitate was filtered, washed with water, and air dried. This salt is practically insoluble.

Analysis.

Calculated	Y = 25.42	C = 20.56	H = 3.74
Found ..	Y = 25.41	C = 20.23	H = 3.78

Yttrium Phenyl Acetate, $Y(C_6H_5 \cdot CH_2COO)_3 \cdot H_2O$.

An excess of phenyl acetate acid was added to yttrium hydroxide and heated. The precipitate formed was filtered while the solution was hot, washed with water, and air dried. This salt was insoluble.

Analysis.

Calculated	Y = 17.38	C = 56.22	H = 4.53
Found ..	Y = 17.42	C = 56.03	H = 4.42

Yttrium Phenoxyacetate, $Y(C_6H_5OCH_2COO)_3 \cdot 3\frac{1}{2}H_2O$.

For the preparation of this compound a solution of yttrium chloride was treated with the sodium salt of phenoxyacetic acid, and the precipitate washed thoroughly with cold water to separate sodium chloride. The product was further purified by re-crystallisation from hot water. This compound was only slightly soluble in cold water.

Analysis.

Calculated	Y = 14.71	C = 47.58	H = 4.66
Found ..	Y = 14.66	C = 47.80	H = 4.50

The phenoxyacetates of Sm, Nd, Pr, La, and Ce were prepared in exactly the same manner as the yttrium salt. They were, however, much more insoluble than the latter, and therefore could not be re-crystallised from water.

Analysis.

Sm($C_6H_5OCH_2COO$)₃ · 3½H₂O.

Calculated	Sm = 22.57	C = 43.20	H = 4.23
Found ..	Sm = 22.61	C = 43.30	H = 4.03

Nd($C_6H_5OCH_2COO$)₃ · 2½H₂O.

Calculated		Nd = 22.47
Found ..		Nd = 22.51

Pr($C_6H_5OCH_2COO$)₃ · 1½H₂O.

Calculated		C = 46.38	H = 3.90
Found ..		C = 46.14	H = 4.03

La($C_6H_5OCH_2COO$)₃ · 2½H₂O.

Calculated		La = 21.82
Found ..		La = 21.83

Ce($C_6H_5OCH_2COO$)₃.

Calculated		Ce = 23.63
Found ..		Ce = 23.88

Thorium Phenoxyacetate.

By working with a neutral solution of thorium the authors found, on the addition of an excess of phenoxyacetic acid, that the thorium was almost quantitatively precipitated. On the other hand, the rare earths behave very differently and are not thrown out of solution, even though a great excess of the acid be added.

This reaction of phenoxyacetic acid on a neutral thorium solution affords a method for the separation of this element from the rare earths.

Durham, N.H., May 26, 1911.

A STUDY OF THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

A MODIFIED PHENOLSULPHONIC ACID METHOD.

By E. M. CHAMOT, D. S. PRATT, and H. W. REDFIELD

IN order that reliable results may be obtained and comparisons with permanent standards shall be possible, we have shown that the phenolsulphonic acid reagent must contain no monosulphonic acid (*Journ. Am. Chem. Soc.*, xxxii., 630; CHEMICAL NEWS, civ., 146 *et seq.*).

After studying many methods of preparation the following is suggested for trial by water analysis.

Preparation of Phenoldisulphonic Acid Reagent.—Dissolve 25 grms. of pure white phenol in 150 cc. of pure concentrated sulphuric acid, add 75 cc. of fuming sulphuric acid (13 per cent SO₃), stir well, and heat for two hours at about 100°.

The reagent thus prepared contains no mono acids, and no tri-acids so far as we have been able to ascertain, and may be heated in contact with water residues for many hours without suffering any development of interfering colours, and is far less sensitive to the interfering action of the substances causing errors than when the old standard reagent is used.

Complete sulphonation usually takes place in from thirty minutes to one hour, but the time of heating suggested is to absolutely ensure the absence of even a trace of mono-acid. The proportion of acids given is such that the viscosity of the final product is sufficiently low to permit measuring the reagent from a 2 cc. pipette, and also prevent the sodification of the reagent should the temperature of the laboratory fall to a little below 15°.

It has been tested during the past year in our student laboratories in large classes, and appears to be a great improvement over the reagent commonly employed.

Theoretically 2 cc. of this new reagent should be capable of taking up 297 parts per million of nitrogen as nitrate. But on trial it has been found that the results are not always reliable when over 50 parts per million are treated, and serious discrepancies arise should the nitrate content be over 80 parts per million. The old reagent is in this respect much worse.

Determination of Nitrates in Water.—First determine the alkalinity, the chlorine, and nitrite content, and the colour of the sample. Should the colour be high decolorise with "aluminium cream."

Measure into an evaporator 100 cc. of the sample, or if the nitrates are very high, such a volume as will contain about 10 parts per million of nitric nitrogen, fairly low colorimeter readings having been found most reliable. Add sufficient 0.04 N or 0.02 N sulphuric acid to not quite neutralise all the alkalinity, then a volume of standard solution of silver sulphate free from nitrate (4.3969 grms. per litre, 1 cc. = 1 cc. of standard silver nitrate solution = 1 mgrm. Cl per cc.), which will precipitate all but about 0.5 mgrm. of the chlorine. Heat to boiling, add a little "aluminium cream," filter, and wash with small amounts of hot water. Evaporate the filtrates to dryness, add 2 cc. of the disulphonic acid reagent, rubbing with a glass rod to ensure intimate contact. Should the residue be compact or vitreous in appearance from much magnesium or much iron present, place the evaporator on the water-bath for a few minutes. Dilute with distilled water, and add slowly a strong solution of potassium hydroxide (10 to 12 normal) until the maximum colour is developed. Transfer to a colorimeter cylinder, filtering, if necessary, and compare with a potassium nitrate or tripotassium nitrophenoldisulphonate standard.

Should nitrites be present in excess of 1 part per million of nitrogen a slight error will be introduced. They should therefore be removed by heating the sample a few moments with a few drops of hydrogen peroxide (Tatlock and Thompson, *Journ. Soc. Chem. Ind.*, 1904, xxiii., 428), free from nitrates, repeatedly added, or dilute potassium permanganate may be added in the cold until a trace of pink appears, and a correction applied to the final nitrate nitrogen reading due to the conversion of the nitrites to nitrates.

Permanent Standards.—Permanent standards made according to the method of the American Public Health Association (*Journ. Infect. Dis.*, 1905, May Sup., 41; Jackson, *Tech. Quart.*, 1900, xiii., 320), using the reagent suggested above, or a series of standards using tripotassium nitrophenoldisulphonate may be employed.

The use of permanent standards with the reagent suggested, containing as it does no mono-acids, introduces no errors, since the reagent does not change its composition with age, the colour of the final product is not influenced by heat, nor by moderate variation in volume of reagent or volume of alkali used. Nor does dilution change the relative value of the standards.

Preparation of Tripotassium Nitrophenoldisulphonate, $\text{C}_6\text{H}_2\text{OK}(\text{SO}_3\text{K})_2\text{NO}_2$.—The pure salt isolated in the progress of the investigation of the nature of the compound producing the yellow colour proved so valuable as a standard for the study of sources of error that much time was spent in an attempt to discover a convenient method for its preparation. None of the methods given in the literature of the nitrophenolsulphonic acids proved successful. As a warning to future investigators it should be recorded that every attempt to sulphonate *o*-nitrophenol with fuming sulphuric acid at 100° resulted in violent explosions. Treatment with fuming acid in the cold for twenty-four hours causes the splitting off of the nitro-group, and an impure phenoldisulphonic acid results.

The only method that has proved practicable thus far in our hands consists in adding, in the cold, to the disulphonic acid reagent described above, the theoretical amount of dry finely powdered potassium nitrate in very small pinches at a time (for every cc. of reagent 0.1076 gm. of potassium nitrate), stirring thoroughly after each addition. The product is then diluted, treated with dry barium carbonate until a deep yellow colour results, filtered, and the precipitate washed with boiling water to dissolve the barium nitrophenoldisulphonate which is but sparingly soluble in cold water. Much of the product sought is lost unless the extraction with boiling water is thorough. Filtrate and washings are united, the barium removed by adding potassium carbonate until alkaline, the solution filtered, and the filtrate concentrated to crystallisation. The yield obtained is about 60 per cent of the theoretical. The salt may be easily purified by re-crystallisation from water. This

method is suggested provisionally until a better one has been devised.

To prepare the standards, the re-crystallised salt thus obtained is dissolved in distilled water, and the solution compared in a colorimeter with a known weight of potassium nitrate treated with the reagent in the usual manner. From the value obtained the proper dilutions for a series of standards are calculated.

Carrying the purification of the tripotassium salt to a point where the theoretical amounts might be weighed out for a set of standards is not recommended, since the products must be dried in a current of carbon dioxide (*Journ. Am. Chem. Soc.*, 1910, xxxii., 635).

Standards prepared as above described were checked repeatedly, both with the chemically pure salts and with potassium nitrate standards during many months, and have as yet shown no tendency to change. During most of this period they have stood in clear glass bottles in diffused daylight. The authors therefore believe that such standards may be recommended as convenient, reliable, and as doing away with the very strongly alkaline standards formerly employed.—*Journal of the American Chemical Society*, xxxiii., No. 3.

ON THE DECOMPOSITION OF THE CERIUM EARTH DOUBLE SULPHATES WITH THE ALKALI SULPHATES BY FUSION WITH CHARCOAL.

By PHILIP E. BROWING and PHILIP L. BLUMENTHAL.

AMONG the best known and chief sources of the cerium earths are their insoluble double sulphates with the alkali sulphates obtained as a by-product in the process for the separation of these earths from the earths of the yttrium group. The problem which has to do with the conversion of these insoluble sulphates into soluble salts of the cerium earths is therefore an important one. The procedure in general use brings about this result by treating the double sulphate with sodium or potassium hydroxide until the cerium earths are converted to the hydroxides, when the alkali sulphates may be removed by washing. The hydroxides are then dissolved in any convenient acid. This method is at best tedious, both in the preparation of hydroxides and the removal by washing of the alkali sulphates. The double sulphates are sometimes digested with hydrochloric acid, and then treated with water, but here also the process is slow in yielding soluble cerium earth material. Or the double sulphates are treated with large volumes of water, frequently stirred, a method even more time consuming than the others.

The work to be described was undertaken to test the application of the reduction by carbon to this problem. This method has been applied to the preparation of soluble barium and strontium salts from barite and celestite (Erdmann-Dunlap, "Introduction to Chemical Preparations," first edition, pp. 27 and 30), and, as we discovered late in our work, is mentioned in connection with some work on cerium over fifty years ago (Berzelius and Hisinger, 1804, *Ann. Chim. Phys.*, l. 252; Beringer, *Liebig. Ann.*, 1842, xlii., 135; Schmidt, *Liebig Ann.*, 1852, lxxxiii., 329). As this early work gave no details or numerical results and contained some statements which our work would hardly bear out we have thought best to give our results.

The material which we used was a crude double sulphate, a technical by-product carrying appreciable amounts of calcium and iron salts together with some sand.

In order to obtain a standard to which to refer results, five portions of 1 gm. each were dissolved in from 300 to 400 cc. of water by frequent stirring for several hours, and the solutions were precipitated in faint acidity by oxalic acid. The oxalate was ignited and the oxide weighed, yielding 0.3897 gm.

Four portions of 1 gram. each were thoroughly mixed with 2 grms. of charcoal, and heated in a covered porcelain crucible over a Bunsen flame for from thirty to forty-five minutes. After cooling, the mass was treated with about 4 cc. of strong hydrochloric acid and 10 cc. of water, when the solution of the cerium earths took place with the abundant evolution of hydrogen sulphide. The residue of the charcoal was filtered off, and the cerium earths in the filtrate were precipitated by oxalic acid in the usual manner. The average of these results, agreeing within a few mgrms., was 0.3908 gram. Three determinations each with 5 grms. of the material and 5 grms. of charcoal heated forty-five minutes gave an average result of 2.021 grms.; and four portions of 10 grms. heated with from 8 to 15 grms. of charcoal from fifteen to thirty-five minutes yielded an average of 4.37 grms. of the oxides. Finally, a portion of 100 grms. was mixed with 200 grms. of charcoal, and heated in a Battersea crucible in a furnace for about one hour. The yield of this experiment was a little over 40 grms. of the oxides.

The conclusion from this work is that the double sulphates of the cerium earths with alkali sulphates are easily decomposed by heating with charcoal into a form easily attacked by hydrochloric acid with the formation of soluble chlorides.

In course of this investigation it was found that the reduction of the double sulphates to sulphides by charcoal was not complete, although the product was readily attacked by hydrochloric acid. Accordingly, several experiments were made to determine the best conditions for forwarding the reducing action. The results appear in the table, and were obtained by determining the amount of sulphate present in the hydrochloric acid extract after carbon fusion, by precipitation with barium chloride.

	Amount of double sulphate taken.	Amount of charcoal used.	Time of fusion.	Sulphate reduced.
	Grm.	Grms.	Mins.	Per cent.
1.	1	2	30	60.5
2.	1	2	60	70.5
3.	1	2	120	91.0
4.	1	2	140	84.6
5.	1	2	240	80.6
6.	1	4	30	59.0
7.	1	4	60	75.4
8.	1	4	30	70.8
9.	1	4	30	64.0
10.	1	4	60	93.7

In Experiments 1 to 9 the heating was carried on in a covered crucible over a Bunsen burner, and Experiment 10 in a furnace. In Experiment 8 the heating was conducted in a current of hydrogen, and in Experiment 9 in an atmosphere of carbon dioxide.

The best conditions seem to involve a moderate excess of charcoal with about an hour's heating.—*American Journal of Science*, xxxii., No 188.

DETERMINATION OF VANADIUM IN STEEL AND IRON.

By B. O. CRITES.

THE determination of vanadium in steel carrying this element in amounts varying from 0.05 per cent to 0.75 per cent has been a problem commanding the attention of many of iron and steel chemists for several years.

The methods given in the earlier editions of books on iron and steel analysis have been found almost wholly impracticable, and those appearing in the more recent literature have neglected to give any very comprehensive idea of their accuracy or limits of accuracy.

Realising the difficulties involved in the estimation of rather minute quantities of vanadium in presence of large

amounts of iron, it is not the intention of the writer to severely criticise the work of other chemists in their efforts to produce satisfactory methods, but it seems that a discussion of the subject might be of interest at least to chemists who have had only limited experience with this determination.

A method said to have been used by J. Kent Smith in his extensive work on vanadium was first tried by the writer; the method in brief was as follows:—

Four grms. of steel were dissolved in sulphuric and nitric acids, the tungsten being separated by the usual methods if present. The nitric acid was expelled by evaporation to the appearance of sulphuric acid fumes, then, after dissolving the salts in water, chromium and vanadium were oxidised with slight excess of potassium permanganate solution. After boiling, the excess of potassium permanganate was reduced with manganese sulphate, and the solution made up to a definite volume, filtered, and an aliquot part of the filtrate taken for titration—chromium being titrated with ferrous sulphate and potassium permanganate, and finally the vanadium with ferrous sulphate and potassium bichromate. The principle underlying the method is that the vanadium is reduced by ferrous sulphate and oxidised by potassium permanganate in dilute solution but not by potassium bichromate.

After a number of attempts the method was finally abandoned. The end reaction being rather indefinite, there frequently was considerable doubt in the mind of the operator whether any vanadium was present or not.

A method described by Blair was next tried (*Chemical Analysis of Iron and Steel*, 6th edit., p. 202). By this method the vanadium was separated from the iron by fusion with sodium carbonate and sodium nitrate, extraction of the vanadium with water and precipitation from slightly acid solution with mercuric oxide and mercurous nitrate. This precipitate was re-dissolved and the vanadium finally precipitated with ammonium chloride as directed. The results were unsatisfactory, and this method was also abandoned.

The writer then endeavoured to work out for himself the details of a method, suggested I believe by Roscoe, which might at least show whether vanadium really was present and the amount.

The method used was as follows:—

Five grms. of steel were dissolved in nitric acid, which was then replaced by hydrochloric acid (tungsten being separated as usual if present), and an ether separation was made to separate the major portion of the iron; the vanadium in the water layer was separated from the iron remaining by large excess of sodium hydroxide, after first replacing hydrochloric with nitric acid. The caustic mixture containing precipitated iron was made up to a definite volume and an aliquot part of the filtrate containing the vanadium acidified, and the vanadium precipitated by lead acetate and sodium acetate. The lead vanadate in turn was filtered off, dissolved in hydrochloric acid, and evaporated to the appearance of fumes after adding a few cubic centimetres of sulphuric acid. Lead sulphate was filtered off and the vanadium in the filtrate was titrated with N/100 potassium permanganate solution.

In order to test its accuracy a standard solution of vanadium was prepared from divanadyl tetrachloride obtained from Eimer and Amend. The solution was standardised as follows:—

The contents of a 4-ounce bottle of vanadium chloride (divanadyl tetrachloride), $2\text{VO}_2 \cdot 4\text{HCl} \cdot 3\text{H}_2\text{O}$, containing 4.051 grms., were diluted to 2000 cc.

Twenty cc. of this solution were withdrawn, 5 cc. strong sulphuric and 40 cc. strong hydrochloric acid added; the solution was boiled down till it fumed strongly, then cooled, diluted to 150 cc. with water, heated to 80°C ., and titrated with standard potassium permanganate solution, of which each cubic centimetre was equal to 0.005 gram iron or 0.004578 gram vanadium.

Measured amounts of this solution were then added to plain carbon steel, also to chrome and molybdenum steel,

and the samples were carried through by the method as described, with the following results:—

Vanadium added. Per cent.	Vanadium found. Per cent.	Difference. Per cent.
0.03	0.03	0.00
0.06	0.06	0.00
0.06	0.05	-0.01
0.13	0.12	-0.01
0.13	0.14	+0.01
0.26	0.22	-0.04
0.26	0.24	-0.02
0.26	0.19	-0.07
0.10	0.09	-0.01
0.10	0.08	-0.02
0.10	0.07	-0.03
0.10	0.08	-0.02
0.10	0.10	-0.00
0.10	0.07	-0.03

Attempts to apply the method on samples to which over 0.30 per cent vanadium was added showed decidedly low results. In such cases it was necessary to fuse the sodium hydroxide precipitate with sodium carbonate and potassium nitrate and determine the vanadium in the water extract, thus complicating the method. While not entirely satisfactory the results were a very considerable improvement on anything obtained so far by other methods used.

Several months later Blair published a method along somewhat similar lines but with a number of improvements and changes (*Journ. Am. Chem. Soc.*, 1908, xxx., 1229). He made two separations with ether instead of one, and omitted the separation of lead sulphate by filtration, this being found unnecessary; a stronger solution of potassium permanganate was also used for the titration. After some practice with the method it was adopted as the best tried so far. The method even in its improved form was still somewhat lengthy and required considerable care in order to obtain anything approaching accurate results. A few of the results obtained are as follows:—

Sample.	Vanadium added. Per cent.	Vanadium found. Per cent.	Difference. Per cent.
Carbon steel.	0.75	0.78	+0.03
Chrome nickel steel . .	0.28	0.25	-0.03
Chrometungsten steel. .	0.195	0.18	-0.015

The principal difficulty was in the analysis of high chromium steels; the chromium seemed to be very difficult to precipitate completely, and would often be carried into the vanadium filtrate and thus complicate matters; also, small quantities of organic matter, probably from the filters used, seemed to affect the results. These difficulties, of course, could be overcome, but they required considerable care.

C. M. Johnson published a method ("Chemical Analysis of Special Steels, &c.," p. 8) about this time which was somewhat on the principle of the method used by J. Kent Smith, and described in the beginning of this paper. He omits, however, the use of manganese sulphate to remove excess of potassium permanganate, and uses potassium ferricyanide in the solution instead of externally as an indicator. In the judgment of the writer this is the most practical method available at present. The method as used in our laboratory is practically the same described by Johnson. Two grms. of steel are dissolved in dilute sulphuric acid, heated with nitric acid, until the insoluble becomes a bright yellow, if tungsten be present, otherwise simply to oxidise the iron. The solution is diluted, brought to boiling, and 3 per cent potassium permanganate solution added until precipitate of manganese oxide remains after twenty minutes' boiling. This is very important, otherwise low results will be obtained. After cooling the solution is filtered through asbestos into heavy suction

flasks, and residue is washed with minimum quantity of very dilute sulphuric acid. (The asbestos should be previously prepared in quantity by ignition in a muffle and washing in water). The volume of the filtrate must not exceed 300 cc. The end reactions in the titrations to follow will be indefinite if solution is too dilute. The filtrate must be perfectly clear.

The titration of the chromium is the next operation; this is conducted as described by Johnson, but it is important to add the standard potassium permanganate until an unmistakable pink persists after thirty seconds' stirring. The oxidation of the vanadium is sometimes a little slow at this point, and permanganate must be added till the operator is certain there is a slight excess. The writer uses a solution of potassium permanganate, each cubic centimetre of which is equal to 0.005 grm. iron. N/10 ammonium ferrous sulphate is used.

The calculation for chromium is as follows:—

cc. KMnO_4 equal to FeSO_4 required for reducing chromium $\times 0.005$ (Fe value) $\times 0.311 \div 2 \times 100$ equals per cent chromium.

The volume of the solution now ready for vanadium titration must not be over 350 to 375 cc. One cc. of a solution of potassium ferricyanide containing 0.020 grm. of the salt in 20 cc. of water is added, then standard ammonium ferrous sulphate (same as used for chromium) till the end-point is reached. It is well from time to time, during the titration, to add a drop or two of the indicator and note whether a green coloration is produced at a point where the drop mixes with the solution.

A blank should always be run on a steel of similar composition to the sample but without vanadium, and proper deduction made. A standard steel of composition similar to the sample, and to which a definite amount of standard vanadium solution has been added, should also be carried along with the unknown.

Inasmuch as the method described above shows accurately the amount of chromium present in the sample, and separate nickel determination, if nickel be present, can readily be made by the dimethylglyoxime or other of the well known methods, there is usually no difficulty in preparing synthetic standards and blank of composition similar to the sample under examination, at least sufficiently close for the purpose. (In this connection it might be well to call attention to the method described by N. M. Randall—*Met. Chem. Eng.*, 1910, viii., 17—for quick estimation of chromium in chrome steels and chrome nickel steels, and also the method of H. Wdowiszewski—*Chem. Ztg.*, xxxiv., 1365; *C. A.*, v., 1378—for chrome in chrome tungsten steels. Both of these methods give excellent results in a remarkably short time).

Sample calculation for vanadium:—

10 cc. FeSO_4 diluted with H_2O and titrated with KMnO_4 required 8.5 cc.

1 cc. KMnO_4 = 0.005 grm. Fe = 0.004578 grm. Va.

Blank required 0.7 cc. FeSO_4 .

Sample required 2.3 cc. FeSO_4 .

$2.3 - 0.7 = 1.6$ cc. FeSO_4 required for the vanadium.

$1.6 \times 0.85 = 1.36$ cc. FeSO_4 (corrected) required for vanadium.

$1.36 \times 0.004578 \times 100 = 0.31$ per cent vanadium.

0.31 per cent + 5 per cent correction = 0.325 per cent vanadium.

A few of the results obtained are given below. There seems to be a tendency towards low results, especially in the higher figures. This may be due to a secondary reaction referred to by W. F. Bleeker in his article on vanadium (*Met. Chem. Eng.*, 1911, ix., 209). "If a solution of hypovanadic acid or its salts be added to a solution containing ferric iron, the presence of ferrous iron is immediately observable. According to this we should expect low results, owing to the mass action of the reduced vanadium upon the ferric iron, giving a test for ferrous iron before the vanadium is all reduced."

The results obtained by the writer were about 5 per cent low. However, if this correction of 5 per cent is made, a very fair agreement is found. The method is quickly carried through and the end-points are sharp.

Sample.	Vanadium (per cent).		Difference (per cent).	Corrected by 5 per cent (per cent).
	Added	Found.		
Plain carbon steel . . .	0.11	0.123	+0.013	0.129
+0.11 per cent vanadium	0.11	0.123	+0.013	0.129
Carbon steel	—	—	—	—
+1 per cent molybdenum	0.55	0.519	-0.031	0.544
+0.55 per cent vanadium	0.55	0.506	-0.044	0.531
Chrome nickel steel . .	0.33	0.309	-0.021	0.324
+0.33 per cent vanadium	0.33	0.309	-0.021	0.324
Chrome tungsten steel .	0.22	0.21	-0.01	0.22
+0.22 per cent vanadium	0.22	0.222	+0.002	0.233
Carbon steel	—	—	—	—
+0.65 per cent vanadium	0.65	0.63	-0.02	0.661
Carbon steel	—	—	—	—
+0.33 per cent vanadium	0.33	0.314	-0.016	0.329
Chrome steel	—	—	—	—
+0.46 per cent vanadium	0.46	0.46	-0.00	0.483
Chrome tungsten steel .	—	—	—	—
+0.529 per cent vanadium	0.529	0.508	-0.021	0.533
Chrome tungsten steel .	—	—	—	—
+0.46 per cent vanadium	0.46	0.42	-0.04	0.441

A number of tests were made by both the Blair and Johnson methods, with results as follows:—

Sample.	Blair method.		Difference (per cent).	Johnson corrected by 5 per cent. Vanadium (per cent).
	Vanadium (per cent).	Vanadium (per cent).		
Chrome tungsten vanadium steel .	0.29	0.287	0.003	0.301
Vanadium steel . .	0.25	0.208	0.042	0.218
	0.25	0.225	0.025	0.236
Vanadium steel . .	0.25	0.225	0.025	0.236
	0.25	0.225	0.025	0.236
Chrome tungsten vanadium steel .	0.75	0.705	0.045	0.74
	0.76	0.72	0.04	0.756
Vanadium steel . .	0.51	0.60	0.01	0.63

Other methods, such as Campbell and Woodham's (*Journ. Am. Chem. Soc.*, 1908, xxx., 1233), in which iron is largely separated from vanadium by converting iron into ferrous sulphate and crystallising out with strong alcohol, and methods described by Auchy (*Journ. Ind. Eng. Chem.*, 1909, i., 455) were either not as readily applicable as the Johnson method or were not successful in the writer's laboratory. Colorimetric methods, such as described by Slawik, were also unsuccessful (*Chem. Ztg.*, xxxiv., 648).

The Johnson method may be used for the determination of vanadium in iron if it be modified to the extent of fusing with alkali carbonate and a little nitrate, the graphite and silica left insoluble when the iron is dissolved, on account of their tendency to carry vanadium. A blank and standard of similar composition should also be run.

Results on vanadium in iron by Johnson's method (modified).

	Vanadium added (per cent).	Vanadium found (per cent).	Difference (per cent).	Corrected (per cent).
Cast iron	0.22	0.21	0.01	0.22
Malleable iron . .	0.23	0.21	0.02	0.22

—*Journal of Industrial and Engineering Chemistry*, iii., No. 8.

Announcement.—Mr. R. Borlase Matthews, Wh.Ex., M.I.E.E., informs us that he is relinquishing his present work as a Consulting Engineer to become Manager to Messrs. Ozonair, Ltd., 96, Victoria Street, Westminster, S.W.

REVISION OF THE ATOMIC WEIGHT OF CALCIUM.*

ANALYSIS OF CALCIUM CHLORIDE.

By THEODORE WILLIAM RICHARDS
and
OTTO HÖNIGSCHMID.

IN an earlier paper concerning the analysis of calcium bromide (Richards and Hönigschmid, *Journ. Am. Chem. Soc.*, 1910, xxxii., 1577), it was shown that the atomic weight of calcium is probably not far from 40.070, this being in all likelihood the minimum, if silver is taken as 107.88. Two series of analyses containing each six individual experiments, carried out according to two methods, gave this number as their mean. The present paper contains a description of further work upon this constant, involving now the chloride instead of the bromide of calcium.

The importance of carrying out systematic experiments upon more than one compound is evident. The constant errors due to possible unknown impurities, as well as to possible defects in method, so surround any work of this kind that no worker with much experience is inclined to trust a single method, even although a single good method is worth more than any number of bad ones. The exact analysis of the chloride might add either essential confirmation of the work on the bromide or important evidence concerning possible flaws. Five preliminary experiments upon the chloride carried out at Harvard thirteen years ago had indeed yielded a result which almost, although not quite, agreed with the figure given above (Richards, *Journ. Am. Chem. Soc.*, 1902, xxiv., 374; *Zett. Anorg. Chem.*, 1902, xxxi., 271); but this preliminary work was done at a time when considerably less was known about the possible errors in working with chlorides than at present. In any case further work upon the chloride seemed to be imperative.

The present paper concerns the determination of the quantitative relation of metallic silver to pure fused calcium chloride. Both of these substances were weighed with great accuracy, and the end-point of the reaction between them was determined in very dilute solution by means of the nephelometer. This method, because of its greater simplicity, is somewhat to be preferred to the weighing of the silver chloride produced from a given amount of calcium chloride. Moreover, the preliminary experiments with the chloride had involved this latter process; therefore the comparison with metallic silver would furnish a new ratio, not hitherto investigated.

We are glad to acknowledge the generous support given this investigation by the Carnegie Institution of Washington.

Preparation of Materials.

Calcium Chloride.—Two different specimens of exceedingly pure calcium carbonate remaining from the preparation of the bromide served as the starting-point of the work on the chloride. Repetition of the details is unnecessary; the only impurities which could have been present besides moisture were traces of ammonium nitrate included in the precipitate. Each of these specimens was dissolved in specially purified hydrochloric acid, which had been boiled repeatedly with small additions of permanganate, and then distilled twice in succession with the help of a quartz condenser. The calcium carbonate had been heated in a platinum dish to a temperature high enough to free it from water and ammonia, but traces of nitric acid may have remained; accordingly, the carbonate was dissolved in hydrochloric acid, in a quartz dish, and the chloride was evaporated to dryness. Subsequently it was crystallised three times, each time being freed as completely as possible from mother-liquor, by means of the platinum centrifuge. Thus, two specimens of calcium chloride were obtained, and to them were given the designations 1 and 2, corre-

* From the *Journal of the American Chemical Society*, xxxiii., No. 1.

sponding to the designations of the carbonate from which they were made.

The mother-liquors from these two chlorides were collected, concentrated, and four times re-crystallised. The mixture of the two specimens thus obtained having a purity not far different from Samples 1 and 2 was designated Sample 3, and served for several analyses.

Silver.—Three preparations of silver were used for this work. Of Sample A the preparation has already been described in the previous paper, and Sample B was made in a similar way by Richards and Willard in their work upon the atomic weight of lithium, already cited. The third, Sample C, was prepared by Dr. C. J. Moore, and kindly given to us for this work. Silver residues, consisting of the three silver halides, were reduced with zinc. The metal was washed, dissolved in nitric acid, and precipitated as chloride. This was dissolved in ammonia, and again precipitated with nitric acid, and once more reduced by means of sugar solution after very thorough washing. The metal thus obtained was melted (by means of the blast-lamp on blocks of lime), etched with nitric acid, and then used as an anode in a dilute silver nitrate solution. A pure silver wire served as a cathode; upon this the silver was deposited in beautiful crystals, and these were carefully washed and melted in a stream of hydrogen in the same way as Samples A and B. The boat of pure lime which served to support the metal was so arranged that the buttons were of various sizes. The pure metal was etched with dilute nitric acid, thoroughly washed, and dried in a vacuum at 500°. Pure nitric acid and other substances were prepared with the usual precautions adopted in the chemical laboratory of Harvard University.

Melting and Weighing of the Calcium Chloride.

The crystallised chloride, like the bromide, cannot be conveniently dehydrated by heating the hydrated crystals, because a crust forms over the liquefied mass. This greatly hinders the evaporation, which is almost invariably accompanied with projection or spattering of drops. On the other hand, as in the case of the bromide, if calcium chloride is placed in a vacuum desiccator at a temperature below its transition-point, 29°, the water leaves the salt with considerable rapidity, and the dried skeleton of the crystal can then be heated to 200° or 300° without danger of loss. In the present case a fortnight's standing in a vacuum desiccator over lime in the best vacuum obtainable by means of a Geryk pump was quite enough for preliminary treatment.

The thoroughly effloresced material was further dehydrated, and finally fused in an apparatus essentially like that used for the melting of the bromide, and almost exactly similar to that used by Richards and Willard for the melting of lithium chloride (Richards and Willard, *Journ. Am. Chem. Soc.*, 1910, xxxii., 25). The calcium chloride was contained in a platinum boat enclosed in a wide quartz tube connected with the familiar Harvard "bottling apparatus," and in this position was gradually brought by means of electrical heating to the temperature of 400°, in a current of nitrogen. After an hour the air in the tube had been displaced, and the salt was almost wholly free from water. Turning the three-way cock then admitted dry hydrochloric acid gas, and as soon as all the nitrogen had been displaced the temperature of the chloride was raised to its melting-point, about 800°. For fifteen minutes the fusion was maintained in the current of acid gas, then this gas was displaced by nitrogen, and the fusion was continued until the greater part of the hydrogen chloride had been given out by the inert element. The product was then allowed to cool rapidly in nitrogen.

During the cooling a hitherto unnoticed phenomenon was observed. As the temperature decreased, the perfectly clear glassy solid, which was at first formed in the boat, was flecked with small white spots. These were caused by the shattering of the glassy chloride as it crystallised, sometimes almost explosively, at the lower temperature, and they gradually spread over the whole surface.

Occasionally some particles of the salt were thrown out of the boat during this process. The effort was made to prevent the change by cooling as quickly as possible. This device was unsuccessful, but we found that the transition could be prevented by heating the salt for a long time in nitrogen. From this fact the conclusion may be drawn either that traces of hydrochloric acid are dissolved by the fused salt, and that these traces hasten the crystallisation, or else that the traces of alkali formed by long ignition in nitrogen retard the crystallisation. The transition phenomenon is accompanied by considerable increase in volume; in one case, indeed, a thin platinum boat was so much increased in diameter by the expanding salt as to make it incapable of admission into its weighing glass—a mishap which naturally caused the loss of that experiment.

After the chloride had been completely cooled and the apparatus again filled with pure dry air, the boat and its contents were pushed into the weighing bottle, and allowed to stand at least six hours in a desiccator in the neighbourhood of the balance. It was then weighed in the usual fashion by substitution.

The platinum boat was attacked somewhat more strongly by hydrochloric acid than by hydrobromic acid. Nevertheless, since the average loss was only 0.08 mgrm. in a single experiment, and since any platinum which had been dissolved probably reverted to the condition of metal in the salt during its fusion in a neutral atmosphere, this complication may be left entirely out of account. The original weight of the boat was taken in each case as the true one.

The experiments with the bromide had already shown us that with a salt as easily decomposed as calcium chloride, it is by no means easy to obtain an exactly neutral product. Accordingly, each specimen of fused calcium chloride was dissolved in a small amount of water, and then titrated with 1/100 normal nitric acid or caustic potash, using methyl-red as an indicator. The departures from neutrality were so slight that they scarcely could have been observed, and could not have been accurately estimated without comparison with a standard solution of calcium chloride known to be neutral. This latter was prepared by crystallising moderately pure calcium chloride, faintly acid, four times from the purest water with thorough centrifugal treatment and all precautions. An equal quantity of this certainly neutral salt was dissolved in precisely the same amount of water as was used for the sample to be tested, and to each was added the same quantity of methyl-red. In most cases the solution of the melted chloride was thus found to be slightly acid, and only when the product had been fused in dry nitrogen for some time did an alkaline reaction appear. Whether the lack of chlorine evidenced by the alkaline reaction was caused by traces of oxygen or water in the nitrogen, or by a reduction to sub-chloride, cannot be absolutely proved; but the former is by far the most likely assumption, therefore it was made in calculation of the results. In this way it was found that the eighth, tenth, and eleventh specimens were precisely neutral, as nearly as this testing could show it. The sixth, seventh, and ninth were slightly acid, requiring 0.10, 0.30, and 0.20 millilitre of 1/100 alkali respectively, whereas the twelfth sample of calcium chloride was alkaline, needing 0.70 millilitre of 1/100 normal acid for its neutralisation. In order to correct for these slight deviations from neutrality a small correction was added to or subtracted from the weight of the calcium chloride according as the calcium was lacking (in slightly acid specimens), or calcium oxide was present as an impurity (in the alkaline specimen). The actual amounts of the corrections in Analyses 6, 7, 9, and 12 amounted respectively to +0.00002, +0.00006, +0.00004, and -0.00020 grm.

It is interesting to note that the sum of all these corrections is a negligible quantity. Their effect is only to improve slightly the agreement of the results. Thus, on the average, the calcium chloride was neutral. This is especially important in its bearing upon other cases, because occasionally, for example, in the case of zinc bromide (Richards and Rogers, *Proc. Am. Acad.*, 1895,

xxxi., 158), indicators give results so unsatisfactory that no clue can be gained as to the neutrality of the fused salt after it has been dissolved. Evidently the amount of acid gas dissolved by the fused salt at a bright red heat is almost negligible, even when the acid gas is present under a full atmosphere's pressure.

The weighings were made upon the same balance and in the same way as has been already described. For the determination of the correction to vacuum of the calcium chloride, it was necessary to determine the weight of air displaced by a given weight of this substance.

The density of fused calcium chloride was determined in the pycnometer devised by Baxter for salts of this kind (Baxter and Hines, *Am. Chem. Journ.*, 1904, xxxi., 221). Toluene having a specific gravity 0.8630 at 25°, compared with water at 25° (that is to say, weighing 0.8605 grm. per cc.), was used as the liquid to be displaced. Two pairs of experiments were made. In the first pair 4.8462 grms. in vacuum of fused calcium chloride displaced 1.9417 grms. in vacuum of toluene, and in another pair 4.1223 grms. of calcium chloride displaced 1.6447 grms. of toluene, the temperature being 25° as before. These two results correspond respectively to values for the density of calcium chloride of 2.148 and 2.156, the mean being 2.152. This value is used in calculating the corrections of the vacuum standard. Because the specific gravity of the gilded brass weights was 8.3, the following vacuum corrections per grm. were applied.

	Density.	Vacuum correction.
Silver	10.49	0.000030
Silver chloride . .	5.56	+ 0.000071
Calcium chloride . .	2.15	+ 0.000415

(To be continued)

SIR JOHN CASS TECHNICAL INSTITUTE.

OPENING LECTURE OF THE COURSE OF INSTRUCTION ON "COLLOIDS."

THE opening Lecture of this course was given by Mr. E. HATSCHEK on Friday, October 6th, when the Chair was taken by Dr. RUDOLPH MESSEL, President of the Society of Chemical Industry.

Dr. MESSEL, in introducing the lecturer, pointed out the importance of the study of colloids in its relation to industries, and hoped that the exceptional opportunity of hearing a course of lectures such as had been arranged would be taken very full advantage of.

Mr. HATSCHEK commenced his lecture by referring to the early work of Thomas Graham on colloids, and then dealt with the subsequent development of the subject as a borderland study between physics and chemistry. The characteristics of colloids were then examined, and an account given of laboratory products that have been prepared, and of the large number of natural organic products which can be dissolved direct to form colloidal solutions such as starch, gelatin, agar, and the albumins. The importance of the subject in relation to industrial problems was next specified, reference being made to the tanning and dyeing industries, the photographic plate and paper industry, the fermentation industries, and the treatment of effluents and sewage.

At the close of the lecture an experimental demonstration of the properties and methods of preparation of some colloidal solutions was given.

A cordial vote of thanks to Dr. Messel for taking the Chair was proposed by the Rev. J. F. MARR, Chairman of the Institute Committee, and seconded by Dr. E. DIVERS, Past-President of the Society of Chemical Industry, who congratulated the Governors of the Institute on the important work they were doing in giving the opportunity for the study of important branches of science which were so intimately associated with the development and progress of industries; the vote was suitably acknowledged by Dr. Messel.

NOTICES OF BOOKS.

The Corrosion of Iron and Steel. By J. NEWTON FRIEND, Ph.D. (Würz.), D.Sc. (Birmingham). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911. (6s. net).

It is remarkable that a subject which is of such great commercial importance as the corrosion of iron and steel should not have been more thoroughly and systematically studied. Isolated researches have been published in abundance, but it has been left for the author to prepare a thorough survey of the whole field, a task which he has performed admirably. His aim in this work has been to collect all the reliable material which is available, to summarise it and criticise it from the point of view of the latest developments of our knowledge, and this aim he has successfully achieved in spite of the great difficulties that have had to be overcome in searching a very large number of periodicals and original papers. The book provides many suggestions for research work, and the author makes it clear exactly in which directions valuable results may be obtained. Some of the work which involves quantitative determinations might quite well be found profitable occupation for young students beginning research work.

The Principal Starches Used as Food. By WALDRON GRIFFITHS, F.R.M.S. Second Edition. Cirencester: Baily and Woods. 1911. (6s. net).

THIS book contains excellent photomicrographs of most of the common starches, with short descriptive notes on their origin and characteristics, and it will be found of the greatest possible assistance in the identification of starches and the detection of adulterations. The illustrations are beautifully clear, and are all magnified 150 times. The author has made some useful additions to the second edition, including illustrations of articles of food, such as Benger's food and Colman's mustard. He now recommends as the best medium for the mounting of permanent preparations of starches, not glycerin and camphor water, but Farrant's gum, which he has found to give very satisfactory results.

The Principles of Bleaching and Finishing of Cotton. By S. R. TROTMAN, M.A., F.I.C., and E. L. THORP, A.C.G.I., A.M.I.E.E. London: Charles Griffin and Co., Ltd. 1911.

THE principles which find application in the bleaching and finishing of cotton goods are thoroughly discussed in this book, in which a systematic account is to be found of modern practice. The author, while laying stress upon the benefits which will accrue to the industry by the adoption of scientific procedure, by no means underestimates the value of rule-of-thumb methods combined with practical experience, and endeavours to give due weight to the contentions of the works' manager, who has very often a poor opinion of scientific practice. The chemistry of bleaching agents is fully treated, and soaps and soap-making are included for consideration, while some space is given to the question of the removal of stains, &c. Finishing and the materials used for filling, stiffening, &c., form the subject of the last part of the book.

Contemporary Chemistry. By E. E. FOURNIER D'ALBE. London: Constable and Co., Ltd. 1911. (4s. net).

IN this book a very interesting summary is given of the whole field of modern chemistry, the latest developments in every branch of the subject being shortly explained. The book is of a type specimens of which were comparatively rare till quite recently; that is to say, well-written and restrained accounts of the advances of the science, free from exaggeration, and thoroughly accurate. Many a teacher who has felt the need of such a work to

put into his older students' hands, the well-informed general reader, and the scientific man who has no special knowledge of chemistry, will all have reason to be grateful to the author for his admirable survey. Special attention is paid in the book to the advances of physical chemistry, which are very satisfactorily summarised.

Elektrochemische Umformer — Galvanische Elemente. ("Electrochemical Converters—Galvanic Cells"). By JOHANNES ZACHARIAS. Wien und Leipzig: A. Hartleben. 1911. (4 marks).

This book gives in a handy form an adequate account of the history, construction, and uses of galvanic cells, and although the author perhaps imagines that they have suffered greater neglect in literature than is actually the case, there is certainly room for the little work, which will be found particularly useful for the attention paid in it to the technical uses of galvanic cells. Cells required for heavy current work are fully discussed, and the treatment of the subject has been made as practical as possible.

Die Zustandsgleichung. ("The Equation of Condition"). By Prof. Dr. J. D. VAN DER WAALS. Leipzig: Akademische Verlagsgesellschaft. 1911.

This lecture was delivered at Stockholm on the occasion of the awarding of the Nobel Prize for Physics to Prof. van der Waals, and its issue in the form of a pamphlet will be particularly acceptable to students of physical chemistry, who will be glad of the opportunity of reading of the steps which led the author to the formulation of the equation of condition. His discussion also of the discrepancies between the results of experiments and the calculated results is full of interest, as well as his attempts to explain the behaviour of binary and ternary mixtures by the aid of the equation.

Chemie der Eiweisskörper. ("Chemistry of Albuminous Substances"). By Dr. OTTO COHNHEIM. Third Edition. Braunschweig: Friedrich Vieweg und Sohn. 1911. (11 marks).

The third edition of this book contains a comprehensive survey of the chemistry of albuminous substances, and any chemist who wishes to learn the facts which have been established, or the theoretical views which have received the widest and most influential support, will find that it gives him full information. Many alterations and additions have been made in this latest edition. For instance, the sections on the secondary degradation products, albumoses and peptones, have been re-written, and a chapter on the albumen ferments has been added, while the physical properties of albumen are treated much more fully than before. Recent work on plant albumens, nuclein acid, and hæmatin is adequately discussed, and references to the literature of the subject have been brought down to the end of 1910.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other is expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 4, July 24, 1911.

Ultra-violet Radiations of Quartz Mercury Lamps.—Victor Henri.—The ultra-violet radiation of a quartz mercury lamp burning in air increases as the tension is raised, the increase being most rapid above 200 watts. Since the action on silver citrate is absolutely parallel to

the sterilising action of the lamp the latter action may be measured by the former. The action on potassium iodide increases more slowly than that on silver citrate. The intensity of the yellow rays increases much more quickly than that of the blue and green rays.

Latent Heat of Fusion and Specific Heat of Fatty Acids.—G. Massol and A. Faucon.—The authors have already pointed out certain anomalies in the specific heats of some fatty acids in the solid and liquid states. They now suggest that the explanation may be that the specific heat in the solid state becomes superior, in the neighbourhood of the melting-point, to the specific heat of the same substance in the liquid state.

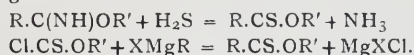
Action of Thionyl Chloride on Metallic Oxides.—G. Darzens and F. Bourion.—As a chlorinating agent thionyl chloride behaves like a mixture of chlorine and sulphur chloride, the products obtained being the same in both cases, as well as the velocities of the transformations and the temperatures at which the reactions begin. Thionyl chloride is a less satisfactory chlorinating agent than a mixture of chlorine and sulphur chloride, because it is difficult to prepare it, and above 440° it decomposes.

Extraction of Gases from Copper and the Determination of Oxygen.—Marcel Guichard.—If copper is converted *in vacuo* into the iodide or oxide it gives up the dissolved gases it contains. From 100 grms. of copper 22–30 cc. of gas may be separated by this method.

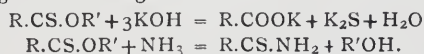
Catalytic Preparation of Substituted Ketohydrofuranes.—Georges Dupont.—Tetramethylketohydrofuran can be prepared by the catalytic isomerisation of acetylenic pinacone by means of a dilute solution of mercuric sulphate. The same process can be applied to other acetylenic γ -glycols. When the substituent radicles are of high molecular weight (unsaturated or aromatic) the reaction is slow, and secondary reactions occur. Tertiary glycols undergo isomerisation more easily than secondary.

Nitration of *o*-, *m*-, and *p*-Nitrobenzoyl-*p*-anisidines.—Frédéric Reverdin.—In the nitration of the nitrobenzoyl-*p*-anisidines with nitric acid the trinitrated derivatives are obtained directly. When benzoyl-*p*-anisidine is treated similarly only a very small yield of trinitro derivative results, and to get better yields it is necessary to nitrate in two stages. Thus the nitro group seems to facilitate the formation of more highly nitrated compounds, but its presence has no influence on the nature of the products as regards the position of the nitro groups introduced into the nucleus. The *o*-nitro compounds are easily saponifiable, which is not the case with the *m*- and *p*-derivatives.

Sulpho-esters R.CS.OR'.—Marcel Delépine.—The sulpho-esters R.CS.OR' can be prepared by either of the following reactions:—



The author has prepared several of these esters in which $\text{R} = \text{C}_n\text{H}_{2n+1}$ and R' is also $\text{C}_n\text{H}_{2n+1}$. They are all pale yellow liquids, insoluble in water and miscible with the usual organic solvents. With alkalis and ammonia they undergo the following reactions:—



These sulpho-esters boil at about 30° higher than the corresponding esters containing no sulphur; they are more dense, and the ethyl and methyl esters of acids containing up to C_5 exhibit oxyluminescence.

Action of Acids on Catalytic Oxidation of Phenols by Ferric Salts.—H. Colin and A. Sénéchal.—Both strong and weak acids decrease the oxidising action of the peroxidasic system ferric salt + hydrogen peroxide. The authors have shown that of the weak acids those which oxidise most energetically are those which form the most stable complex compounds with the iron salts, as, for example, tartaric acid, citric acid, and oxalic acid.

α -Methylenon. New Ketone Derivative of Camphor.—R. Locquin.—When camphor is treated with Caro's reagent a lactone, $C_{10}H_{16}O_4$, is formed. In presence of sulphuric or phosphoric acid it gives up CO_2 , and an unsaturated ketone, $C_9H_{14}O$, is obtained. This ketone is a tetramethylcyclopentanone, which, adopting Tiemann's nomenclature, may be called α -methylenon.

Vol. cliii., No. 5, July 31, 1911.

Spectrum of Beryllium and its Bands in Different Sources of Light.—Lecoq de Boisbaudran and A. de Gramont.—With the aid of photography the authors have detected a new band in the indigo in the spectrum of beryllium; it is decidedly fainter than the bands in the green and the blue. If the band spectra of beryllium and aluminium are photographed on the same plate a striking resemblance between them is observed; thus the β -beryllium band 5056.4 corresponds to the β -aluminium band 5079.5, the α -beryllium band 4709.0 corresponds to the α -aluminium band 4842.4, and the γ -beryllium band 4428.0 to the γ -aluminium band 4648.1.

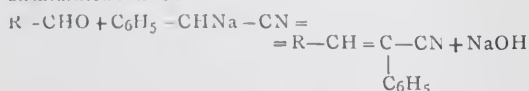
Molecular Weight of Thorium Emanation.—M. S. Leslie.—The rate at which thorium emanation passes through a small aperture can be used to determine the molecular weight. Adopting Hahn's figures the molecular weight would be 210–201, and from Bronson's results 203–194. A difference of 1 per cent in the activity gives a difference of 5 per cent in the molecular weight, which, however, must be about 200.

Fluorescence of Vapours of Alkaline Metals.—L. Dunoyer.—The metals to be investigated were enclosed in exhausted glass tubes, and an arc lamp was used as the source of light. The sodium spectrum begins to appear at 290° , but the D-line is visible at about 210° . The fluorescence of sodium, if it is pure, is not green but light yellow. The purple fluorescence of potassium appears at 215° , and becomes very bright at 320° . Rubidium vapour becomes fluorescent at about 180° , the colour resembling that of potassium. The fluorescence of caesium begins at 350° ; it increases slowly above this temperature, the glass of the tube meanwhile turning brown. The fluorescence of rubidium apparently varies with the temperature, becoming orange at 400° ; it appears to consist of two bands.

Metallurgy of the System Selenium-antimony.—H. Pélabon.—The microscopic examination of mixtures of selenium and antimony leads to the same conclusions as those which are drawn from the determination of the fusibility curves, viz.:—1. That for certain proportions of the two constituents the liquid mixture can be formed of two phases of nearly the same densities. 2. That the only compound which can be obtained by fusing the elements together is the selenide, Sb_2Se_3 .

Action of Bromine in presence of Aluminium Bromide on Cyclohexanol and Cyclohexanone.—F. Bodroux and F. Taboury.—In presence of aluminium bromide, bromine acts energetically on cyclohexanol, giving hexabrom-benzene. Cyclohexanone is also attacked in the same conditions, the chief product being tetrabromocyclohexanone. Compounds insoluble in alcohol are also formed, and an oily liquid, the yield of the latter being greater the longer the duration of bromination.

Action of Anisic and Piperonylic Aldehydes on the Sodium Derivative of Benzyl Cyanide.—F. Bodroux.—Anisic and piperonylic aldehydes react energetically with the sodium derivative of benzyl cyanide, giving an unsaturated nitrile:—



t the same time part of the aldehyde is transformed into e corresponding acid.

Atti della Reale Accademia dei Lincei.

Vol. xx., (1.), No. 12, 1911.

Formation of Solid Solutions of Metals by Diffusion in the Solid State.—G. Bruni and D. Meneghini.—By measuring the increase of the electrical resistance of a nickel wire covered with copper the authors have shown that the two metals diffuse into one another, and form a solid solution. They have now extended their investigations to wires of gold and copper, and gold and silver, and have confirmed their previous results.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xliii., No. 12, 1911.

Determination of Active Hydrogen in Organic Molecules.—Bernardo Oddo.—In this paper the author describes a gravimetric method of determining active hydrogen in organic molecules, depending upon the evolution of ethane when the organic compound reacts with ethyl magnesium iodide. The apparatus consists of two small flasks, one containing the organic compound and the other the ethyl magnesium iodide in isoamyl ester; the whole is weighed, the two substances are brought into contact, and the ethane is allowed to escape, and the loss of weight is determined. The percentage of hydroxyl groups is obtained from the formula $x = OH \text{ per cent} = 56.6178 \frac{C}{P}$, where C = the amount of ethane and P is the weight of substance used. The number of hydroxyl groups present in the molecule is given by $y = \frac{C \cdot D}{P \cdot 30.04}$, where D is the molecular weight.

Preparation of Isoprene from Terpene Hydrocarbons.—H. Staudinger and H. W. Klever.—Isoprene can be prepared by heating to high temperatures the diluted vapours of limonene or dipentene. Dilution can be effected either by adding large quantities of indifferent gases such as nitrogen, or else by rarefaction. It is best to heat by means of a metallic spiral heated electrically. Yields up to 60 per cent can be obtained at low pressures. The isoprene thus prepared is quite pure.

MEETINGS FOR THE WEEK.

TUESDAY, 17th.—Faraday Society, 8. "The Paragon Electric Furnace and Recent Developments in Metallurgy," by J. Hårdén. "Progress in the Electro-metallurgy of Iron and Steel," by D. F. Campbell. "The Hering 'Pinch Effect' Furnace," by E. K. Scott.

WEDNESDAY, 18th.—Microscopical, 8. "Structural Details of *Coscine-discus asteromphalus*," by T. W. Butcher. "The Wheat Plant," by A. Flatters. "New British Enchytraëids," by Rev. H. Friend. "Instantaneous Exposure in Photomicrography," by W. Bagshaw.

THURSDAY, 19th.—Chemical, 8.30. "Action of *Allium sativum* or Garlic Juice on Lead and Mercury," by M. Banerjee. "*p*-Methoxysalicylaldehyde and its Occurrence in the Root of a Species of *Chlorocodon*," by E. Goulding and R. G. Pelly. "The Alkaline Condensations of Nitrohydrazo-compounds," by A. G. Green and E. A. Bearder. "Simple piece of Apparatus for Sublimation *in vacuo*," by H. Christopher. "Dehydration of Crystals," by J. B. Firth. "The Diphenylcarbamid-oximes," by F. P. Dunn. "Some Properties of Phenylisopropyl Ketone" and "New Stereoisomeride of Cyanodihydrocarvone," by A. Lapworth and V. Steele. "Action of Hydrogen Cyanide on Carvone Hydrosulphide," by V. Steele. "Experiments on the Walden Inversion—Part VII., Action of Phosphorus Pentachloride and of Thionyl Chloride on Optically Active Hydroxy-acids and Esters," by A. McKenzie and F. Barrow. "Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amine Bases," by P. Neogi. "Studies of Ammonium Solutions—Part I., An Ammonium Electrode," by R. E. Slade.

THE CHEMICAL NEWS.

Vol. CIV., No. 2708.

THE INFLUENCE OF CONSTITUTION ON THE MOLECULAR VOLUMES OF ORGANIC COMPOUNDS AT THE BOILING-POINT.*

By GERVAISE LE BAS, B.Sc.

(Continued from p. 153).

The Configuration of the Poly-halogen and other Similar Paraffin Derivatives.

THESE data are historically interesting, because they were shown by Stadel to support the view that molecular volumes are not additives simply because isomeric compounds may sometimes have very dissimilar volumes. Beyond the influence which these facts at the time had on the weight given to Kopp's molecular volume theory, and the vague notion that the differences somehow or other are connected with differences in constitution, little additional significance has been given them. (For data, see Table II., *prox.*).

The results may now be stated as follows:—

1. When two or more halogen or other atoms or groups are attached to the *same* carbon atom, the volumes are normal and comparable with the volumes of members of the paraffin series.

2. If two or more atoms or groups are attached to *different* carbon atoms, and are thus more or less distributed, there is a considerable diminution in volume, which is greater the more symmetrical is the distribution.

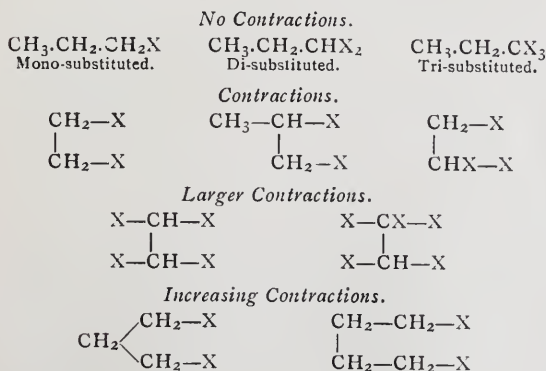
3. The result appears to be independent of the nature of the atoms or groups, so far as observation has been made, and these include Cl, Br, I, and OH.

4. The contraction for the $\alpha\alpha$ -compounds is zero, for the $\alpha\beta$ -compounds 2 or 3 units, for the $\alpha\gamma$ -compounds greater still. It follows that the contraction increases the more the substituents are separated.

5. If there are two or more substituents in the α -position the contractions will increase with the number of substituents in the β - or other positions.

The last observation indicates that the contractions are due to the substituents, but the other atoms or groups may be affected. Moreover, there appears to be some fundamental difference between two neighbouring carbon atoms. The observation in (4) seems to contradict the evidence which may be adduced in favour of the action of residual affinity, but this is really not the case, and is explained below.

The compounds may be written as follows:—



It will be seen that the hypothesis of mutual action between the substituents fully fits the facts, and that the greater contraction of the $\alpha\gamma$ - and $\alpha\delta$ - as compared with the $\alpha\beta$ -compounds is due to the curvature of the hydrocarbon chain, whereby the two substituents which are not directly connected by means of valencies are brought near by their mutual attractions. The amount of the contractions will then evidently depend on number of groups enclosed in the incomplete ring. Compare propylene dichloride and trimethylene dichloride.

Compounds with a constitution and configuration like the above are intermediate between straight-chain compounds and completed rings.

It may not be out of place to bring forward as evidence in favour of the curved configuration of these di-substituted compounds the facility with which ring formation occurs by the action of reagents, as Baeyer has done for the γ - and δ -lactones. Cases which occur to one are the formation of the cycloparaffins from the di-halogen compounds, the cyclic oxides from the glycols, the imides from the diamines, and so on. The physical evidence given above shows that the curvature is probably general in the case of the di-substituted paraffins, and that the two substituents are brought nearer by this means.

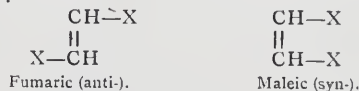
If two carbons are connected by an olefine linking two isomers are possible, the fumaric or anti-compounds and the maleic or syn-compounds. According to our hypothesis the latter should possess the smaller volumes owing to the attraction between the substituents. It should be mentioned that the monovalent H-atoms never occasion contractions like the above.

Data are lacking for the boiling-point, but it is certainly a fact that the densities at 20° of the maleic esters are higher than those of the fumaric esters (Knops).

	Fumaric ester.		Maleic ester.		Δ .
	d_{20} .	M.V. ₂₀ .	d_{20} .	M.V. ₂₀ .	
Ethyl ..	1.0520	163.5	1.0692	160.9	-2.6
Propyl ..	1.0220	182.0	1.0290	180.7	-1.3

The acids have not been examined, but no doubt the difference would be still greater. The amount of the contraction evidently depends on the unsaturation of the groups, and this is evidence in favour of our hypothesis of the action of residual affinity.

The reason for the above contractions is shown by the following:—



Differences in relative position, other than the above, would, however, not make any difference in the volume. For instance, the densities at 20° of tartaric and racemic acids are the same. The density of mesotartaric acid which possesses the OH groups in the syn position would no doubt be higher and the volume smaller.

Constitutive Effects in Ring Compounds.

Contractions due to the presence of Unsaturation Side Chains. (See Table III., *prox.*).

Having discussed the constitutive effects in open chain compounds, it remains to consider ring compounds. The constitutive influences may be connected (a) with the nucleus, and (b) with the side chains. Reserving for the present our treatment of the effect of ring structure, we shall deal first with mono-substituted, then with di-substituted compounds. An interesting fact connected with the former is that if the side chain consists of a group which is unsubstituted, or involves the presence of residual valencies, or generally may be supposed to give rise to residual affinity, the sum of the atomic volumes, even allowing for the special constitutive influence of ring structure, is larger by several units than the observed value.

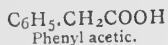
* A Paper read before the British Association (Section B), Portsmouth Meeting, 1911.

Such groups are: $-\text{OH}$, $-\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}:\text{CH}\text{COOH}$, $-\text{NO}_2$, NH_2 , $-\text{CH}_2\text{Cl}$.

Exceptions: Single Cl, Br, I, and possibly CN.

If, however, the H-atoms be substituted by alkyl groups, and the residual affinity thus for the most part got rid of, the contraction is either very much diminished, or, what is more general, it completely disappears.

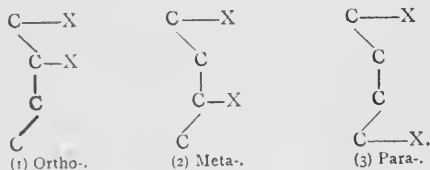
It is also interesting to find that the magnitude of the effect depends apparently on the distance of the unsubstituted group from the nucleus, for the contraction for benzoic acid is much greater than for either phenyl propionic or cinnamic. Phenyl acetic acid is probably intermediate.



There can be no doubt that a constitutive effect of the nature shown above is due to a mutual action between the nucleus and the side chain, as a result of the action of residual affinity of the latter, or of both.

The Mutual Interference of the Two Substituents in the Benzene Nucleus. (See Table IV., *prox.*.)

The di-substituted products of benzene are each divisible into three classes:—



in which the substituents occupy the $\alpha\beta$, $\alpha\gamma$, $\alpha\delta$ positions respectively. If our hypothesis be correct the contractions should diminish with the apparent mutual separation of the substituents, because there is no possibility of distortion or curvature of the ring. Such a result would be opposite to the constitutive effect in open chain compounds. The data show that the ortho-compounds are always the smallest and the para-compounds the largest. It is again significant that the latter are again normal or made up additively from the volumes of the nucleus and side chain, assuming that the latter possesses that volume which is usual in open chain compounds. The ortho-compounds thus exhibit a constitutive effect, the meta-compounds in a lesser degree, while the para-compounds are outside the range of each other's influence. This constitutive effect is the result of attractions between the neighbouring substituents. It does not, however, follow that under the action of reagents such effects as the bridging of the ring may not occur. We are at present concerned with the disposition of certain groups in the pure liquid.

The Constitutive Effect Due to Ring Structure.

The effect of ring structure on molecular volumes has never been studied with any degree of completeness, nor are the amounts of the contractions known for more than a few cases. Moreover, as will be seen, an examination of molecular volumes at common temperatures like 0° is ill adapted to bringing out the true value of the constitutive effect. The results are contradictory to those obtained at the boiling-point.

It may be said as a general conclusion that whenever a compound assumes ring structure, the molecular volumes are subject to very considerable contractions, the magnitude of which are dependent on the number of groups in the ring, or more exactly on the number and nature of the included atoms, and also on the complexity of the ring system.

A considerable number of experimental data are available, and these have been discussed in various papers

published in the *Philosophical Magazine* and the *CHEMICAL NEWS* since 1907. The needs of a growing theory, however, demanded new and more extended data. As a preliminary it has been sought to calculate the volumes at the boiling-point by means of the densities at 0° or 20° . A relation has been found which gives results to usually within 1 per cent of the observed values. It has been verified by an examination of available data for organic compounds, and also of eighteen or twenty inorganic compounds which have been determined by Thorpe and others.

The relation is—

$$\frac{T-t}{T} = C \frac{d_t - d_T}{d_t};$$

d_T and d_t being the densities at t , and T the boiling point; C is a number which is nearly the same for a large number of substances, including ring compounds. The value is 0.450, and the only modification necessary is to add 0.023 for every CH_2 or equivalent group in the side chain.

The most interesting series of ring compounds is that of the cycloparaffins up to octamethylene. (See Table A.)

It should be observed that the olefins possess volumes at the boiling-point which are proportional to the valency numbers, so that no allowance must be made for unsaturation as such.

The numbers representing the contractions form a regular series, evidently dependent on the complexity of the rings. If the differences obtained at 0° be tabulated and studied a very different result is obtained to the above. The volumes of the cycloparaffins are subtracted from those of the paraffins, and $2 \times 3.1 = 6.2$ subtracted from the differences for H_2 . (See Table B.)

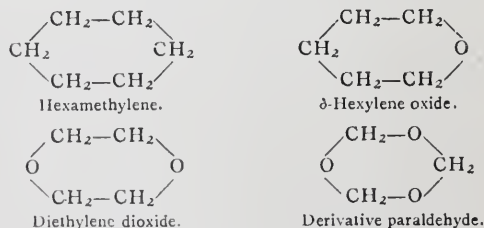
It is observed that the results at 0° and the boiling-point are not the same and are incompatible. Moreover, the differences at 0° are somewhat irregular. The contractions at the boiling-point form a regular curve, increasing somewhat more rapidly than in simple proportion with the number of groups. This again denotes mutual action of the components of the ring. The contractions at the boiling-point are considerably larger than at 0° , and rise to a higher value.

By means of the formula many other compounds have been studied, the amounts of the contractions being verified in many cases by results for known and analogous compounds. The number of cases studied are:—Three membered rings eight compounds, four membered three compounds, five membered fifteen compounds, six membered two dozen or so, while for seven and eight members one member each—the cycloparaffin. The results agree with those of Table B.

Some very interesting cases have been studied, *e.g.*—

A series of polymethylene oxides, sulphides, imines, and cycloparaffins.

Cases of gradual substitution of methylene by other elements, *e.g.*—



The contraction is similar in all the above, *viz.*, 16.0.

A large number of benzene and hydroaromatic derivatives, including the chief types of terpene compounds. Cases like oxides, lactones, and anhydrides, which give results in conformity with the types of rings which characterise them.

Complex rings have also been studied, *e.g.*, naphthalene, quinoline, and various terpenes like camphene,

TABLE A.—Volumes of the Cycloparaffins.

Olefin.	Formula.	M.V.	Δ .	M.V.	Formula.	Cycloparaffin.
Propylene ..	C_3H_6	66.6	- 6.4	60.2	C_3H_6	Trimethylene
Butylene ..	C_4H_8	88.8	- 8.8	80.0	C_4H_8	Tetramethylene
Amylene ..	C_5H_{10}	110.0	- 12.0	98.0	C_5H_{10}	Pentamethylene
Hexylene ..	C_6H_{12}	132.5	- 16.0	116.5	C_6H_{12}	Hexamethylene
Heptylene ..	C_7H_{14}	154.8	- 20.8	134.0	C_7H_{14}	Heptamethylene
Octylene ..	C_8H_{18}	177.6	- 26.4	151.2	C_8H_{18}	Octamethylene

TABLE B.—Comparison of the Contractions at 0° and the Boiling-point.

Compound.	N.	Δ_0 .	Augm.	$\frac{\Delta_0}{N}$	$\Delta_{B.P.}$	Augm.	$\frac{\Delta_{B.P.}}{N}$
C_3H_6	3	—	—	—	-6.4		-2.13
C_4H_8	4	-5.1		-1.20	-8.8	2.4	-2.20
C_5H_{10}	5	-8.9	3.8	-1.78	12.0	3.2	-2.40
C_6H_{12}	6	-9.6	0.7	-1.60	-16.0	4.0	-2.66
C_7H_{14}	7	-12.1	2.5	-1.72	-20.8	4.8	-2.97
C_8H_{16}	8	-15.0	2.9	-1.87	-26.4	5.6	-3.30

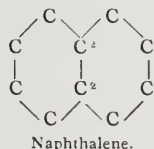
pinene, and fenchene, including other bridged ring compounds like pinol, cineol, tanacetine, and the alkaloids nicotine and tropidine.

The contractions are in most cases about 30.0

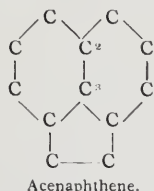
Three and four ring systems are:—Sesquiterpenes 45 (approx.), anthracene 48.3, acenaphthene 43.0, diterpenes 60.0 (approx.).

A more detailed account of this work is in preparation. The magnitudes of the contractions are obviously very useful for purposes of elucidation of chemical structure.

One peculiar feature of complex rings is that the contraction is similar if the double ring is condensed and if it consist of two separate rings, thus—



would possess a similar contraction to two separate six-membered rings, and—



would possess a similar contraction to two single six-membered rings and one five-membered ring.

The result is that those C-atoms which are common to two or three rings respectively have to be counted over twice or thrice. They are thus subject to double and treble contractions, and the particular atoms are correspondingly small. The effects thus overlap in condensed rings, but are, in consequence, additive. This feature is important since it enables us to distinguish condensed from uncondensed rings in practice, for if the amount of the contraction is known the quotient of this and about 2.45, the contraction for one group gives the number of groups. If this number correspond with the number of C-atoms in the formula or is less, the compound possesses a ring system with the rings uncondensed. If the number of groups calculated be greater than the number of C-atoms in the formula, the ring system is condensed. The difference gives the number of

atoms common to the two or three rings. These facts are often sufficient to state exactly the constitution of the compound.

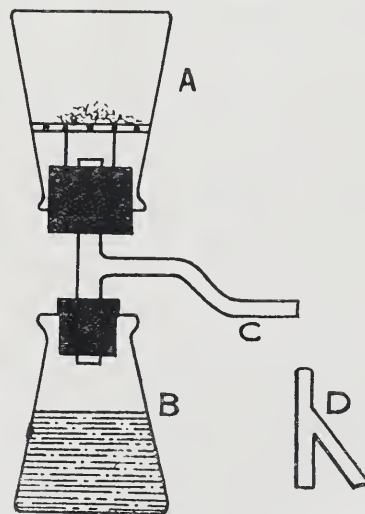
To be continued).

A SIMPLE SULPHURETTED HYDROGEN APPARATUS.

By E. RATTENBURY HODGES.

INTO two conical flasks, preferably of thick glass, perforated rubber stoppers are tightly fitted; the upper flask A is provided with a light wooden grid or stout cork disk full of holes, the wood or cork having been previously soaked in hot melted paraffin wax.

On this grid the iron salt rests. The other flask B is charged with acid. The two vessels are connected by a



T-piece, whose projecting arm curves downward. When the acid and ferrous sulphide are in their respective flasks, it is then only necessary to cautiously turn the apparatus upside down in order to get the flow of gas. Obviously this cheap and simple instrument would also serve for the production of hydrogen, carbon dioxide, and other gases.

If the apparatus be so turned as to keep the curved tube upright, no acid will enter it. However, D would be a better form of delivery tube.

COMPOSITION OF A FALSE SILVER COIN.

By J. NEWTON FRIEND and WILLIAM DAVISON.

A FLORIN having come into our possession which looked rather dull and lead-like, we decided to analyse the same, and thereby determine whether or not the coin was genuine. The metal lacked the usual "ring" which characterises genuine coins when thrown on to a hard surface; it bent out of shape somewhat more readily than usual, and when strained still further snapped, exhibiting considerable brittleness. Qualitative analysis showed that the coin consisted essentially of aluminium and antimony, the merest traces of lead, arsenic, and iron being present. The actual figures obtained are:—

	Per cent.
Aluminium	53.40
Antimony	46.38
Lead	Trace
Arsenic	Trace
Iron	Trace

The Technical College,
Darlington.

FUSIONS.

By H. C. PRITHAM.

IT is not the writer's intention to claim anything new in the following article, but merely to give his method of fusing any material for analysis in the laboratory. From observation I have found few chemists using any such method, and, furthermore, have had the pleasure of instructing quite a number of very excellent analytical chemists in the details of the same.

I have noticed in visiting many laboratories from Boston to San Francisco that the majority use the old method of fusing at a high heat and then running the fusion up around the sides of the crucible. Some allow the fusion to settle and cool somewhat, then put the bottom of the crucible in water and allow the button to "pop" loose. While I do not question the accuracy of such methods, I do claim that there is an unnecessary waste of time. In a commercial laboratory, or a factory one for that matter, time is costly—very costly. The most insistent demand on the head chemist is "When can we have results?" and the telephone is kept busy until they get them, too.

Any method of running a fusion around a crucible to cool takes time and care to perform the operation, and in the subsequent digestion in hot water the fusion dissolves slowly, and if, as sometimes happens, considerable of the fusion collects in a hard mass in the bottom of the crucible, it certainly takes time and patience to get it dissolved out. With the following method all this is avoided. The crucible is almost entirely clean from the fusion and the dissolving of the bottom is very fast. The minimum of time is required to transfer the liquid fusion to the digestion in hot water. Many times in a commercial laboratory or a cement plant one has to fuse twenty or thirty samples of clay or other material in the morning, and as a rule has about four platinum crucibles to do the work in. The sooner the chemist can make a fusion and get a clean crucible back the more time he will have to sleep that night. Moreover, the wear and tear on the platinum is much less. The sudden chilling of a crucible in cold water, or the squeezing in of the sides in order to loosen a fusion is not beneficial; the platinum gets brittle and loose. Considering the present price of 43 dols. an ounce, it is of interest to take care of the crucibles.

My method is to take a shallow 5-in. evaporating dish and bend up a clay triangle so as to set in the centre of this. In the triangle put a 50 cc. nickel crucible so that it is held solid, and leave about an inch space between the bottom of crucible and dish. Fill the dish with cold water up to the triangle, and you are ready for business.

When the fusion is finished raise the heat for a minute or two, remove the cover, and at once pour the fusion into the nickel crucible by taking up the platinum crucible in the forceps on one edge. This can be done very quickly and easily with practice. Almost all the fusion will pour out and will solidify at once. Have a casserol ready half full of hot water, pick up the nickel crucible in the forceps, tap it lightly on the desk, and dump the button into the casserol. Keep the casserol covered. The action of the hot water on the hot button will disintegrate it. Add the platinum crucible and cover, and after a few minutes take them out and rinse off. If necessary, rinse in acid into a beaker, using this acid when the fusion is made acid for evaporation. Acid should not be added, however, until the fusion is well dissolved. The button will leave the nickel crucible clean, but if desired it can be rinsed in hot water. If this is done be sure to have the crucible perfectly dry before pouring the next fusion. A little water will cause rather startling results when the hot fusion is poured in on it.

In conclusion, I would call attention to the fact that a blast lamp is not necessary for fusions, contrary to most text-books. A good Bunsen will give all the heat needed except in a few iron ores. The heat should be low until the fusion is well under way. In no case should the practice of turning on a blast lamp for fifteen minutes be put up with.—*The Chemical Engineer*, xiii., No. 4.

REVISION OF THE ATOMIC WEIGHT OF CALCIUM.*

ANALYSIS OF CALCIUM CHLORIDE.

By THEODORE WILLIAM RICHARDS

and
OTTO HÖNIGSCHMID.

Concluded from p. 184).

Precipitation and Gravimetric Titration.

THE weight of silver supposed to be exactly equivalent to each fused and weighed portion of calcium chloride was dissolved with all ordinary precautions in nitric acid. After dilution the liquid was heated, in order to expel nitrous vapours, and then diluted further to a litre. The chloride solution also, after being tested for its neutrality, was diluted to a litre in the three-litre Erlenmeyer flask which had served originally for its dissolving. The silver solution was added little by little to the chloride solution in the dark room; and the flask was then closed and the mixture shaken for a short time in order to mix thoroughly the two solutions. Violent shaking was not practised, because this causes the precipitate to cohere, and prevents the washing out of included chloride or silver. On the following morning the mixture was shaken energetically for about fifteen minutes, and then packed in ice in order to diminish the solubility of silver chloride by lowering the temperature and thus to increase the accuracy of the determination of the end-point. The question as to whether silver or chloride was in excess in the supernatant liquid was then determined by means of the nephelometer in precisely the same way as had been used in the alreazý often quoted work on the atomic weight of lithium, where the details are to be found. The test was made only after the chloride solution had remained for twenty-four hours in the cooling-bath. Seven determinations gave the results shown in the accompanying table.

It is to be noticed that the three samples of silver gave results essentially identical, and that the three specimens of calcium chloride were also practically alike, within the limit of error in experimentation. The quantity of material used, although not differing greatly in the individual experiments, seems to have produced no noticeable effect on the results. It is worthy of remark that the series of

* From the *Journal of the American Chemical Society*, xxxiii., No. 1.

RATIO OF CALCIUM BROMIDE TO SILVER—FINAL CALCULATIONS.

No. of experiment.	Sample of calcium chloride.	Sample of silver.	Corrected weight of calcium chloride in vacuum.	Weight of silver in vacuum.	2Ag : CaCl ₂ = 100 : x.	Atomic weight of calcium.
VI.	I.	A	4.60350	8.94908	0.514410	40.075
VII.	II.	B	4.82401	9.37780	0.514407	40.074
VIII.	II.	C	4.81846	9.36688	0.514415	40.076
IX.	II.	C	5.29799	10.29911	0.514412	40.076
X.	III.	C	5.40550	10.50832	0.514402	40.073
XI.	III.	C	5.24539	10.19715	0.514398	40.073
XII.	III.	C	5.34110	10.38328	0.514394	40.072
			35.53595	69.08162	0.5144054	40.074

determinations was an uninterrupted one, no experiments having been rejected from it.

These analyses thus lead to the number 40.074 for the atomic weight of calcium, if silver is taken as 107.88 and chlorine as 35.457. The probable error of this series of results is smaller than that of either of the two series with bromide, being only 0.0004. The maximum deviation from the mean is only 0.002 in the atomic weight of calcium, which corresponds to about 1 part of calcium chloride in 55,000. The agreement is therefore as good as could be expected in work of this kind. The reason for the improvement over the previous series is undoubtedly to be found in the increase of experience with which this last problem was attacked. The knowledge gained in earlier work was of great service in the later determinations.

The Atomic Weight of Calcium.

Four series of determinations concerning the atomic weight of calcium have been carried out in the Harvard laboratory. The first series, executed in 1897 and 1898, claimed to be nothing more than a preliminary treatment of the subject, and was undoubtedly subject to several minor possibilities of error which modern knowledge could have eliminated. The present authors in their recent paper on the analysis of calcium bromide contributed the next two series, and the analysis which has just been described completes the list. The results of these four series with their respective "probable errors" are entered in the following table:—

From the ratio 2AgCl : CaCl ₂ ..	Ca = 40.085 (± 0.0011)
From the ratio 2AgBr : CaBr ₂ ..	Ca = 40.070 (± 0.0007)
From the ratio 2Ag : CaBr ₂ ..	Ca = 40.070 (± 0.0007)
From the ratio 2Ag : CaCl ₂ ..	Ca = 40.074 (± 0.0004)

Average for the atomic weight of calcium Ca = 40.075

This average, 40.075, is almost exactly identical with the last of the four series, and may be taken as the atomic weight of calcium, if silver = 107.88 and chlorine = 35.457. Possibly silver is really as low as 107.87; if this is the case, the atomic weight of calcium would become 40.072. It would appear that Hinrichsen's value, 40.142 (*Zeit. Phys. Chem.*, 1901, xxxix., 311), is in all likelihood distinctly too high. A repetition of the first, slightly divergent series, given in the above table, has already been begun; but the work has been interrupted by the necessary departure of one of us for Europe. It will be continued in the near future.

Summary.

The most important results recounted in the present paper are as follows:—

Pure calcium chloride was prepared by dissolving very pure carbonate in very pure hydrochloric acid by crystallisation of the product. Three samples gave consistent results, showing the material to have been pure.

Fused calcium chloride was found to suffer transition into a more bulky form on cooling, if traces of hydro-

chloric acid are present. The glassy fused salt, obtained by the fusion of a neutral or slightly alkaline salt, was found to have the density 2.15 at 25°.

By gravimetric titration 35.53595 grms. of fused neutral calcium chloride were found to require 69.08162 grms. of silver in seven consecutive experiments, corresponding to an atomic weight for calcium of 40.074 if silver is 107.88.

This value equals almost exactly the average of all the Harvard work upon the subject, 40.075, and may be taken for the present as the most probable atomic weight of calcium.

EFFECT OF IGNITION ON SOLUBILITY OF SOIL PHOSPHATES.

By G. S. FRAPS.

IT is known that ignition of the soil increases the quantity of phosphoric acid dissolved therefrom by acid. Stewar uses this as a method for estimating the organic phosphoric acid of the soil (*Bull.* 145, Illinois Experiment Station). He extracts the original soil and the ignited soil with 12 per cent hydrochloric acid, and assumes that the increased quantity of phosphoric acid secured originates from organic phosphates.

The object of the work here reported was to study the effect of ignition upon mineral phosphates such as may occur in the soil.

Method of Work. The quantity of phosphate containing 0.1 gm. phosphoric acid was weighed into a platinum dish and ignited for ten minutes, at a low red-heat. It was transferred, dish and all, to a bottle, 200 cc. of 12 per cent hydrochloric acid added, allowed to stand twenty-four hours, filtered, washed with hot water, and made up to 500 cc. Phosphoric acid was then determined in 200 cc.

Another series of experiments were made, in which the ignited phosphate was digested five hours at 40° with 500 cc. of N/5 nitric acid.

Results.

The results of the experiments are reported in the table. Ignition increased the solubility of the phosphoric acid of these phosphates decidedly. With fifth-normal nitric acid about ten times as much phosphoric acid is dissolved from the ignited phosphates as from those not ignited. With the strong acid, ignition rendered practically completely soluble all the phosphates which were not already completely soluble in this solvent.

It is evident that no analytical method for organic phosphoric acid can be based on ignition. If the strong acid dissolves all inorganic phosphates, then any method which determines the remaining phosphoric acid will determine the organic phosphoric acid. If the strong acid does not dissolve all the inorganic phosphates (and we have evidence that it does not) then the remaining inorganic phosphates will be rendered partly soluble in the acid by the ignition, so that the ignition method would not be accurate.

Phosphoric Acid Dissolved from Ignited and Original Minerals.

In Percentage of the Quantity of Phosphoric Acid Used).

Laboratory number.	With 12 per cent hydrochloric acid.		With N/5 nitric acid.	
	Original mineral.	Ignited mineral.	Original mineral.	Ignited mineral.
240 Wavellite .	—	100	4·8	80·7
721 Wavellite .	19	100	4·5	97·5
726 Wavellite .	18	100	2·0	58·0
714 Dufrenite .	100	100	4·8	35·5
718 Dufrenite .	86	96	8·0	75·0
716 Variscite .	26	100	12·0	100·0
724 Triplite ..	100	100	—	—

Phosphoric acid is not the only constituent of the soil whose solubility in acid is increased by ignition. We have examined twenty-five soils, and ignition increases the oxide of iron and alumina dissolved by the acid from every one of them. The increase is greater in some instances. For example, in soil 3368, ignition increased the acid-soluble oxide of iron and alumina from 2·63 to 8·48 per cent, and in soil 1361 from 1·25 to 6·50 per cent. Full details of this work will be published in *Bull. 135* of the Texas Experiment Station.

Summary and Conclusions.

1. Ignition increases about ten times the solubility of the phosphoric acid of wavellite, dufrenite, and variscite in fifth-normal nitric acid.
2. Ignition renders variscite, dufrenite, and wavellite almost completely soluble in 12 per cent hydrochloric acid.
3. Ignition of the soil will probably render inorganic phosphates soluble in acid, and therefore is not a method for estimating organic phosphoric acid.
4. Ignition of the soil renders considerable quantities of iron and aluminium oxides soluble in acid.—*Journal of Industrial and Engineering Chemistry*, iii., No. 5.

PROGRESS IN THE ELECTRO-METALLURGY OF IRON AND STEEL.*

By DONALD F. CAMPBELL.

THE development of electro-metallurgical methods of smelting is probably the most important advance of recent years, both in electrical and metallurgical science. Although the last few years have seen the introduction of few fundamental principles or processes, the all-important evolution from the laboratory to the commercial stage has, in many cases, been accomplished, more especially in the electrothermic processes to which I would refer, and increase of efficiency and reduced cost of production are the problems receiving most attention at the present time.

Generally speaking, power supply is one of the chief factors in this work, but this is the case in a varying degree, and we must consider briefly the influence of the various commercial factors which may produce the maximum profit in any electro-metallurgical enterprise, to understand intelligently the distribution of the industry in various parts of the world.

The potential wealth of Scandinavia as regards water-power supply and transport facilities is probably unrivalled, and consequently the industries in which power is of prime importance are highly developed, such as the manufacture of nitrates, cyanamide, carbide of calcium, ferro-silicon, and the smelting of refractory lead-zinc ores and iron ore. The power-cost factor in the manufacture of these products is high, and would be quite prohibitive in any country such as England, where the price of electricity is at least three times that of the usual cost in Scandinavia.

The waterfalls and torrents of the Alps in Savoy and Switzerland are another source of cheap power, and consequently the production of ferro-alloys and aluminium is profitably carried on at Neuhausen, L'Argentière, and elsewhere, the latter industry being especially favoured by the proximity of immense deposits of bauxite, the ore from which all aluminium is obtained, which occur near Marseilles.

As types of water-power stations may be mentioned Trollhättan in Sweden, which already has 50,000 h.p. in operation, generated at 10,000 volts and 25 periods by four turbines of 12,500 h.p. capacity each, and four units of similar capacity are nearly completed. This station has been built by the Government for general distribution, and power is supplied at 44s. per horse-power year for electric smelting. The usual power station constructed exclusively for furnace work is, however, of a different nature, and another typical example may be taken from L'Argentière, where 40,000 h.p. is developed by machines of 850 k.w., each generating at the voltage required, and direct connected to the furnace bus-bais without switches, &c., the control being entirely at the water-gate of the turbine. Niagara Falls is another important source of power of medium price, and the centre of several industries, notably the manufacture of aluminium, carbide, ferro-alloys, and carborundum.

In the case of the electro-metallurgy of iron and steel, there are many other important factors in addition to the cost of power; but the two questions of smelting iron ores to make pig-iron or steel direct from ores and the melting and refining of steel possess fundamental differences, and must accordingly be considered separately.

The reduction of iron ores has only made headway in Scandinavia and the Pacific Coast of America, and, with the possible exception of Central Canada, these are the only points at which it is likely to find general application for many years. Both these countries are without coking coal, but have large quantities of timber available for charcoal. On the Pacific Coast pig-iron is brought thousands of miles by train from the Eastern States or by sea from China, although water-power is plentiful, iron ore of remarkable purity is found, and wood slabs and sawdust produced as a waste product from the saw-mills are available for charcoal manufacture.

In Sweden large deposits of ore still remain, though the price of charcoal is increasing as the supply decreases, owing to the exhaustion of the forests and the growing demand for wood-pulp. The iron-masters, having foreseen a time when it will be impossible to make pig-iron profitably unless some reduction in the consumption of charcoal per ton of pig-iron can be made, devoted about £20,000 for the erection of works to evolve some process to overcome this unsatisfactory state of affairs. The electric furnace solves this difficulty, as charcoal is required only as a reducing agent and not as a source of heat, so that the consumption is reduced two-thirds; in other words, the available charcoal will profitably smelt more than double the quantity of ore by the development of the enormous possibilities of the waterfalls, provided the power can be produced at 33s. per horse-power year under the conditions and prices now prevailing for charcoal and pig-iron. This development will be closely watched with the greatest interest by political economists, as the balance of power in Europe is influenced by the distribution of the world's iron and steel trades; and it is interesting to note that the prestige of nations varies with the importance of this fundamental industry, as is exemplified in the high position of Britain and the development of iron and steel trades of Germany in recent years.

That this new development will strengthen Sweden, especially in the north, is beyond doubt; but there is another important development which will undoubtedly restore the balance to a great extent, namely, the electric refining of steel, which can be carried on in any country, irrespective of exceeding low cost of power.

* A Paper read before the Faraday Society, October 3, 1911.

The position of Sweden has been dependent to a great extent on the fact that the pig-iron made from local ores and charcoal is of exceptional purity and commands a high price, because it was impossible to refine the steel made from impure materials. The use of the electric steel furnace is removing this preference enjoyed by the Swedish manufacturer owing to the natural resources of the country, and pure steel can now be made by the Germans from the impure ores in Luxemburg, by the French in Lorraine, or the British in Cleveland.

The results of smelting operations at Trollhättan in Sweden, and Heroult in California with 2000 k.w. furnaces, at Dömnarvet with 3000 k.w. furnaces, prove conclusively that this type of furnace can compete profitably with the small Swedish charcoal blast furnaces if power costs less than 33s. per kilowatt year at the present state of our practice, and important improvements are to be expected in this as in the case of the steel furnace, which is in a more advanced state of development. This figure for the cost of power is quite reasonable, and leaves a margin of profit for the power company where general conditions are favourable. In California the price of power is about 50s. per kilowatt year, but the cost of ore is lower and that of pig-iron higher than in Sweden. It is interesting to note that the furnace developed independently at Heroult, California, and in Sweden is almost identical, as may be seen in the illustrations. The greatest credit is due to the careful and persistent work of the engineers in charge of the operations at these three pioneer works, and such men as Noble and Ljungberg, who have had the foresight and courage to supply the necessary capital to develop this process from a theoretical to a commercial and profitable basis. The furnaces are two or three phase, and have three, four, or six electrodes. The troubles at present experienced are the difficulty of maintaining a circulation of gas in the furnace without excessive electrode consumption or other means of forcing the heat up the charge in such a way as to increase the active zone in the furnace—in other words, to avoid an excessive concentration of heat near the electrodes, and properly to utilise the rich gas given off from the furnace. Minor improvements of this character are being constantly made, and the process generally improved thereby.

The refining of steel by electricity is, however, of even greater interest, both on account of its high state of development, wide application, and its economic importance in Britain. A few years ago the best steel could only be made from the purest minerals, the domestic supply of which is approaching exhaustion. Now pure steel of excellent quality can be made from inferior ores such as those of Cleveland and Lincolnshire, and the price of power in England is sufficiently low to make this a profitable operation.

Statistics show that the rate of growth of electric refining has been more rapid than that of other important processes, and the output of electrically refined steel for five important countries has arisen from approximately 30,000 tons in 1908 to 120,000 tons in 1910, and a further increase will probably be maintained this year.

Perhaps this is due to its varied application, as it has been already found profitable for the manufacture of many classes of tool and special steels and castings. But the question that is now before progressive steel-makers is of much greater significance. Will the electric furnace, which has already absorbed over 30 per cent of the high class steel trade, be applied generally, in conjunction with the basic or acid Bessemer converter, to compete with open-hearth steel in the matter of cost? At present it can only compete with best acid open-hearth steel for price, though in quality it is superior to any steel made by these methods, and consequently its general adoption would mean an improvement in quality which is now so necessary to meet the requirements of modern engineering. Many steel-makers think it impossible, but German and American engineers are giving this problem the most serious consideration, and several 20-ton electric furnaces are now

being erected with complete confidence to prove the economy of this very application as a duplex process.

Owing to the nature of the native ore deposits, Germany is dependent on the basic Bessemer process for the production of cheap steel. Sixty per cent of the output is made by this process, but it is now realised that the steel so produced is not sufficiently reliable for modern requirements, and some improvement in quality is essential if this process of Thomas and Gilchrist is to survive, and several plants are now adding electric refining to solve this difficulty, which is so serious to them because 97 per cent of the steel output is by basic processes, 60 per cent being Bessemer and 37 per cent open-hearth. In America there is no basic Bessemer production, but the basic open-hearth process accounts for 59 per cent of production. If the electric furnace is generally adopted as an adjunct of the basic Bessemer process, its application to Germany's output of steel alone would absorb about 250,000 k.w. per annum and mean a wide application of electricity.

The generation of power for steel works generally, and electric furnaces in particular, must be briefly discussed. The load factor is high, and the power factor above 0.9 in furnace work, so that all machines can operate at high efficiency. In a 100,000 h.p. central station at one of the works of the United States Steel Corporation, where 2000-k.w. furnaces are used, gas-engines using blast furnace waste products and supplemented with steam-engines are the prime movers. Similar furnaces are to be used in a most interesting works, which are unique in England, because a large rolling mill, blowing engines, electric furnaces, steel furnaces, and auxiliary motors will all be driven by the gas from the company's blast furnaces and coke oven gases without the burning of any other coal or fuel. Under such conditions the cost of power is under 0.25d. per kilowatt hour.

In the case of steam turbines, which are also used in England for furnace work, the cost is from 0.4 to 0.5d., while corporation supplies are also used at the high figure of 0.65d. per kilowatt hour.

The current used in steel refining may be of single-, two-, or three-phase, and of any commercial periodicity. Furnaces of 2000 k.w. capacity are working with frequencies from 25 to 60, though modifications of design are necessary for high periodicity if a good power factor is to be maintained.

The variations in load have been stated to be a serious trouble, and when melting scrap on circuits used for lighting purposes this may be the case, though precautions may be taken to overcome this trouble, and with properly designed machinery these shocks can be practically absorbed, and the variations of voltage kept within the necessary limits, even with small central stations.

Progress both in the metallurgical and mechanical details of the steel furnace is continuous. Two years ago the power consumption used for melting and refining cold scrap under best conditions was 750 kilowatt hours per ton, but one furnace in England has required a power consumption of only 575 kilowatt hours per ton for the last 527 tons manufactured. The difficulties of making good electrodes have been one of the principal difficulties, but now a material of excellent quality is obtainable from several manufacturers, and the consumption of carbons has undoubtedly been reduced 50 per cent during the last three years by improvements in manipulation and material, and breakdowns are no more frequent than in the case of the old-established processes under experienced men.

The operation and design of a steel furnace requires experience if satisfactory results are expected, and difficulties always occur when any new design or problem is being worked out. The usual operation is the removal of sulphur, phosphorus, and oxides from steel which may or may not be previously melted, and the addition of carbon and various alloys. The progress of these reactions is shown diagrammatically in an illustration, the first part being carried on with an oxidising slag and the second under reducing conditions.

It must be remembered that a large number of engineers of the highest technical training and international experience are constantly engaged in improving furnace design and metallurgical methods on behalf of powerful industrial organisations. Careful and expensive experimental work has been going on for years, and many of the furnaces and processes, which are continually being patented and published, have been tried and abandoned by those controlling large electrochemical works. Improvements must be looked for by increasing the general efficiency of the best processes we have at the present time rather than by radical changes in furnace construction.

In all questions of design it is essential to bear in mind first and foremost the metallurgical requirements, and the electrical considerations always must take a purely secondary place. The neglect of this principle has caused the failure of the majority of the numerous furnaces that in recent years have been described in technical journals, but abandoned because they are based on incomplete theoretical data with little or no commercial practice, whereas the most successful electric steel furnace of to-day follows as closely as possible the best basic open-hearth practice with the simplest possible application of electrical heat energy.

A COLORIMETRIC METHOD FOR VANADIUM IN IRON AND STEEL.*

By CHAS. R. McCABE, Engineer of Tests, the Lima Locomotive and Machine Co., Lima, O.

A COLORIMETRIC method for vanadium in iron and steel has lately been adopted in the laboratory of the Lima Locomotive and Machine Co., Lima, O. It requires from three-quarters of an hour to two hours, according to the nature of the material, and has the advantage of permitting the determination of tungsten, nickel, and chromium in the same portion used for the vanadium determination.

The colour employed is that obtained by adding hydrogen peroxide to an acid solution of vanadium. Before proceeding to a description of the method, it is necessary to direct attention to certain properties of vanadium on which it is based.

The colour of vanadium with hydrogen peroxide is subject to many disturbing influences. It is masked and otherwise influenced by iron; strong acids deepen it, and when present in large amounts impart a tinge of orange; an excess of hydrogen peroxide partially bleaches it, and finally any vanadium not in the most highly oxidised form does not yield any colour at all. In view of these facts it need hardly be said that the conditions under which the colour is produced must be rigorously controlled.

Vanadium, like other metals, may be separated from the bulk of iron by means of ether, but unlike nickel or copper cannot be further purified by the ammonia precipitation of iron. Ammonia does not precipitate vanadium existing alone in solution, but when any considerable quantity of iron is present, the precipitate produced by ammonia retains vanadium with great tenacity. This reaction may be a precipitation of vanadium as a vanadate of iron, although it apparently partakes of the nature of occlusion. These properties of vanadium make it possible to obtain all the vanadium from a vanadium steel with a limited quantity iron and free of nickel and chromium when these metals are present. This is accomplished by making the ether separation of the bulk of the iron in the usual way, and following with an ammonia precipitation, having oxidised chromium when present after the ether separation is made.

It is evident that if we dissolve the ferric hydrate carrying vanadium in hydrochloric acid and decolorise the ferric salt in some manner, that we have obtained the vanadium in form for a quantitative development of the

colour in hydrogen peroxide; that is, in such form that it may be compared with a standard. It is further evident that this standard must contain nearly the same amounts of iron, acid, and hydrogen peroxide as the sample being analysed.

The essential features of the method are as follows:—Two grms. of vanadium steel are dissolved in hydrochloric acid, the iron oxidised with nitric acid, and an ether separation made. The amount of iron in the acid solution is purposely increased in order to have sufficient to occlude all vanadium when precipitated. In the absence of chromium, this acid solution containing vanadium is diluted and precipitated with ammonia. If nickel is present, a second ammonia precipitation is made. The ferric hydroxide carrying vanadium is dissolved in a limited amount of hydrochloric acid, the solution decolorised by addition of hydrofluoric acid, and the vanadium colour produced by addition of hydrogen peroxide. The quantities of acids and hydrogen peroxide must very carefully be measured. The colour thus produced is compared with a standard.

When chromium is present, it is oxidised by potassium chlorate before precipitation with ammonia, and so passes into solution along with nickel.

The standard is an artificial one. It is prepared by mixing ferric chloride and hydrochloric acid in such a way as to imitate the solution of the ferric hydroxide in hydrochloric acid following the ammonia precipitation, decolorising with hydrofluoric acid, and adding a quantity of a standard solution of vanadium pentoxide. The colour is then produced by hydrogen peroxide, and the standard diluted as required. Both standard and test must contain the same quantity of acids and hydrogen peroxide, which may be accurately and quickly measured by small pipettes. The solution required for this method follows:—

1. A dilute solution of hydrogen peroxide. The amount required in a determination is 1 cc. of the 2.6 per cent solution furnished by the dealers. It is therefore convenient and also more accurate to employ a solution of such strength that an amount which may be measured by a small pipette will contain this desired quantity. For example, dilute 100 cc. of the 2.6 per cent solution to 500 cc., and use 5 cc. in a determination.

2. Hydrofluoric acid. The amount used in a determination is $\frac{1}{2}$ cc. of the usual chemically pure product. It may be diluted for the purpose, or a small graduate may be used, first filling to a convenient point with water, then measuring the acid by adding drop by drop from the paraffin bottle.

3. A hydrochloric acid solution of ferric chloride containing one-tenth of a gm. of iron and an amount of acid equivalent to 1½ cc. of the strong 1.2 sp. gr. product in each 5 cc. Dissolve 50 grms. of the salt (crystallised with 6 molecules of water) in 300 cc. of dilute hydrochloric acid (1:1), and dilute to 500 cc.. Or the solution may be prepared by dissolving a plain steel in nitric acid, precipitating with ammonia, filtering, washing, and dissolving in hydrochloric acid, and diluting as required.

4. A neutral standard solution of vanadic acid. Vanadic acid, or vanadium pentoxide, cannot at present be obtained on the market. Its preparation, however, is not difficult. Select a good grade of vanadate of iron containing about 60 per cent of V_2O_5 , 38 per cent of Fe_2O_3 , and 2 per cent of SiO_2 . This may be obtained of the Primos Chemical Co., Primos, Delaware County, Pennsylvania. Dissolve 5 grms. in 100 cc. of strong hydrochloric acid in a beaker by aid of heat. Add 20 cc. of water and 1 cc. of hydrofluoric acid. Filter into a separatory funnel. Add 50 cc. ether, and shake under a hydrant in the usual manner. Draw off the lower layer, and discard the ethereal solution. Return the acid solution to the funnel, decanting from the silicious matter which settles in the bottom of the solution. Make a second ether separation of the iron, and return the acid solution to the funnel, again decanting from silicious matter. Finally, make a third separation of iron, and filter the acid solution. The

* From the *Chemical Engineer*, xliii., No. 6.

vanadium solution, now free of iron and nearly free of silica, is purified of ether by heating on a steam or electrical heating appliance, or by blowing air through it. The quantity of contained ether is so large that it cannot be safely brought near a flame.

Dilute in a 600 cc. beaker to 250 cc., and heat to boiling. Add cautiously a small amount at a time, about 10 grms. of potassium chlorate. Follow with a sufficient quantity (from 25 to 35 grms.) of potassium carbonate to nearly neutralise the solution, but be careful not to over neutralise the solution. A copious precipitate of hydrated vanadic acid is thrown down when the right degree of acidity is reached. Dilute and boil. Filter through a 15 cm. filter-paper, wash thoroughly with hot water, and apply suction to collect the precipitate in a cake. Separate from the filter-paper, place on a watch-glass, and dry in an oven at about 100° C. As the moisture is being expelled, break the mass into small particles from time to time with a glass rod. Finally, when entirely dry pulverise and preserve in a vial for use.

If the vanadium pentoxide is dried at too high a temperature, or if it is not broken up in the partly dried state, it becomes very hard and difficult to pulverise.

Weigh accurately about two-tenths of a gm. of the vanadium pentoxide into a small beaker. Add 36 cc. water and 4 cc. strong hydrochloric acid. Heat gently, and when all is in solution add 4 cc. ammonia, sp. gr. 0.96. Dilute so that 1 cc. contains 0.0002 vanadium, or an amount corresponding to 0.01 per cent in a 2 gm. sample of steel.

This standard solution of vanadium pentoxide assumes a yellow colour upon addition of the ammonia. In time it becomes colourless, but this change has no influence on the strength of the solution or results obtained by its use.

In preparing the standard vanadium solution, an important essential is to employ the minimum amount of hydrochloric acid in dissolving the vanadium pentoxide. There are several reasons for so doing. Much hydrochloric acid reduces vanadium pentoxide to dioxide upon application of heat, and this must be avoided by using hydrochloric acid as dilute as practicable, and heating gently. Again, much acid in the standard must be avoided on account of its influence on the colour. The ferric chloride solution contains the correct amount, and it is necessary to be able to use any required amount of the vanadium solution without appreciably affecting the acid content of the standard. Nor is it practicable to use a liberal quantity of acid in dissolving the pentoxide, and neutralise the excess, since chlorine in any form beyond a certain amount retards the decolorising action of hydrofluoric acid on ferric chloride.

The correctness of the vanadium standard is, of course, absolutely necessary to satisfactory results in this method. It must be remembered that the vanadic acid as precipitated contains a very large quantity of water, and time must not be called too soon on the drying process. The directions as given yield a strictly chemically pure vanadium pentoxide, but, nevertheless, it is advisable to test its purity by ignition or otherwise.

This method as practised by the writer is applicable to nearly all steels and irons. Absence of chromium greatly simplifies the process. It is suggested that one first attempting to use this method select a standard vanadium steel free of chromium. The Bureau of Standards furnishes a plain vanadium steel containing 0.15 per cent vanadium which may be used to gain experience with the method. The details of the method follow:—

Absence of Chromium.

Weigh 2 grms. of the vanadium steel into a dish or beaker, add 40 cc. strong hydrochloric acid, and heat until the steel is dissolved. Add 5 cc. nitric acid (sp. gr. 1.2), and evaporate to about 10 cc. Pour into a separatory funnel, and wash the dish or beaker with hydrochloric acid (1:1), using a small quantity at a time until the volume of the solution amounts to 20 cc. as shown by a mark on the

funnel. Add 50 cc. of ether free of alcohol, stopper tightly, and shake under a hydrant. Allow to stand in the rack until the two layers separate completely. Draw off the lower layer into a 25 cc. graduate, and take 1½ cc. of the ethereal solution. This method of making the ether separation yields approximately one-tenth of a gm. of iron in the acid solution, an amount which occludes vanadium satisfactorily and yet permits of the separation of nickel when present.

Transfer the acid solution to a 400 cc. beaker, dilute to about 225 cc., and bring to a boil. Or, to save time, have some boiling hot water at hand and dilute with it. Add ammonia to the boiling solution cautiously, with brisk stirring; when iron is precipitated, add 10 cc. ammonia in excess. Continue to boil for one-half minute. The iron thus precipitated carries with it all the vanadium, while manganese is almost entirely left in solution. If the iron is precipitated in the cold solution and the solution then boiled, a certain amount of manganese is occluded. Upon attempting to dissolve the precipitate in the necessarily limited amount of acid, the manganic hydroxide remains undissolved, and retains some vanadium.

Filter the ferric hydroxide with its occluded vanadium on an 11 cm. filter-paper. Wash with hot water, and if nickel is present, dissolve in hot dilute hydrochloric acid back into the beaker in which precipitation was made, and make a second precipitation in the same manner, filtering, and washing as before. In the absence of nickel a single precipitation of iron by ammonia is sufficient. This is the case in the Bureau of Standards, sample No. 24.

Open the filter-paper containing the ferric hydroxide and vanadium in a dish. Add 3 cc. hydrochloric acid (1:1), and about 7 cc. water. Rock the dish, heating moderately, until the precipitate was dissolved. Do not attempt to hasten solution by stirring or macerating the paper with a rod, as objectionably large quantities of fibre become suspended in the solution. The solution is clear if the occlusion of manganese is avoided by making the precipitation in the manner described.

Pour the solution into the tube in which comparison is to be made. Camp's manganese comparison tubes are recommended for the purpose. It is convenient to use two of the large glass stoppered tubes, since the standard can thereby be prepared without the necessity of pouring from one to another.

Wash the dish and paper with cold water, and pour washings into the tube containing the solution. Dilute to about 40 cc., and add ½ cc. of hydrofluoric acid in dilute form or by use of a small graduate as described. A complete decolorisation of the iron salt occurs. If the solution is warm, this effect is not complete until it is cooled. Presence of chlorine beyond the stipulated amount retards the decolorisation of iron, while an unusually large amount of iron may require more hydrofluoric acid. But if directions are carefully observed, no trouble need be experienced at this stage.

To the colourless solution add 5 cc. of the dilute hydrogen peroxide solution containing 1 cc. of the 2.6 per cent reagent. Upon mixing the brown vanadium colour appears.

The standard is prepared as follows:—Into the other tube place 5 cc. of the ferric chloride solution containing one-tenth gm. of iron and 3 cc. dilute (1:1) hydrochloric acid. This solution is similar to that obtained when the ferric hydroxide is dissolved in the dish. Add a quantity of the neutral standard vanadium solution, accurately measured from a burette. The amount to be used depends upon the vanadium content of the test; 15 cc. is the best quantity to take at first. Dilute to 40 cc., and bleach the solution with hydrofluoric acid, as in the test, and add hydrogen peroxide, using exactly the same quantities of acid and hydrogen peroxide as were used in the sample being analysed. Dilute to five times as many cc. as there were cc. of the standard vanadium solution taken, and mix. Compare colours in the usual way. One-fifth of the number of cc. to which the test is diluted is

hundredths per cent vanadium. For example, if 15 cc. of the neutral vanadium solution are used in the standard, dilute same to 75 cc. If the volume of the test is 82 cc. when the colours match, the percentage of vanadium in the sample is 0.164.

As in colour methods generally, the standard must contain approximately the same amount of the substance being determined as the test sample. The range of negligible departure is about 0.03 per cent. Hence, the number of cc. of standard vanadium solution is conveniently taken in multiples of five. In the example cited, if the test is diluted to 95 cc. before the colours match, another standard is prepared containing 20 cc. of the vanadium solution, and diluted to 100 cc. Upon again comparing colours, the test is found to be slightly dark, requiring further dilution. It is best to use a minimum amount of vanadium solution at first, since any necessary change in standard is effected by merely adding more of the vanadium solution. In the example given, it is sufficient to add 5 cc. of the vanadium solution to the standard, and dilute to 100 cc.

Presence of Chromium.

When chromium is present in a vanadium steel, it is all found in the ammonia precipitate following the ether separation. Hence, some modification of the method is necessary, since upon solution of the precipitate in hydrochloric acid the chromic chloride imparts a green colour to the solution. The plan followed is to oxidise chromic oxide to chromic acid following the ether separation, thus avoiding the precipitation of chromium by ammonia. The details are as follows:—

The bulk of the iron is removed by the ether separation, which is made in the same manner as when chromium is absent, except that the volume of the acid solution is received into the 400 cc. beaker, and $1\frac{1}{2}$ cc. of the ethereal solution received into a small graduate, and added to the acid solution in the beaker. This is merely to avoid increasing the bulk of the acid solution by the washing which is necessary when it is received into a graduate.

Evaporate the acid solution, which need not exceed 20 cc., almost to dryness in the beaker. This is accomplished rapidly, and with a good quality of glass-ware, without danger of breakage, by constant agitation of the uncovered beaker on a hot plate or over a bare flame. The solution is carried down to 1 cc., and 50 cc. of strong nitric acid added. The beaker is covered, and the solution boiled until fumes are all expelled, and the solution is a clear green. To the boiling nitric acid solution enough potassium chlorate (about 2 or 3 grms.) is added to precipitate manganese and oxidise chromium. Continue boiling a moment or two, then dilute to about 225 cc. with boiling hot water. Add cautiously to avoid loss by violent ebullition. Then add cautiously, to the boiling solution, with vigorous stirring, enough ammonia to precipitate iron, and 10 cc. in excess. Boil for half a minute. The chromium being oxidised to chrome acid is not precipitated, while the iron occludes vanadium as before.

Filter the precipitated manganese, iron, and occluded vanadium on an 11 cm. filter-paper, and wash with hot water. In addition to manganese, this precipitate contains a notable quantity of nickel, when this metal is present, and also a certain amount of occluded chromic acid, which cannot be removed by washing. A second ammonia precipitation is therefore necessary. Dissolve the precipitate in hot dilute hydrochloric acid back into the beaker in which precipitation was made, dilute to about 225 cc., and make a second precipitation by ammonia, stirring the boiling solution vigorously and adding 10 cc. of ammonia in excess as before. Filter on an 11 cm. filter-paper, and wash with hot water.

The iron precipitate being now freed of nickel, manganese, and all but a trace of chromium, is treated as described when chromium is absent. It is to be observed at this point that upon addition of hydrofluoric acid the

decolorisation of the ferric chloride generally reveals a small quantity of chromic acid in solution. If the ammonia precipitations have been properly carried out, this retained chromium is not a source of error, the hydrogen peroxide converting the yellow colour into blue, which rapidly fades. This change, however, is not apparent, being masked by the brown vanadium colour. If through improper management of the ammonia precipitation the amount of chromium in the solution is increased, its colour is not thus easily destroyed.

(To be continued).

NOTICES OF BOOKS.

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. WALTER NERNST, Ph.D. Revised in accordance with the Sixth German Edition by H. T. TIZARD. London: Macmillan and Co., Ltd. 1911. (15s. net).

THIS work on theoretical chemistry is well known in this country, and has established for itself an enviable reputation for lucidity of treatment and completeness. The clear descriptions of simple experiments in physical chemistry suitable for the illustration of lectures on the subject are a valuable feature, which marks the book out from other similar treatises. In the third English edition, which has been prepared from the sixth German edition, the reader will naturally turn with special interest to the discussion of the author's work on thermodynamics, and will find that his new theorem on the maximal work and the heat of reaction is fully explained, and the deductions to be drawn from it are pointed out. The author's recent work on specific heats at low temperatures is also discussed, and a new chapter has been added on radio-activity.

The Soil Solution. By FRANK K. CAMERON. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1911.

THIS small book represents an attempt to put before the student the problems of soil chemistry in their widest aspect. The author points out the commercial importance of the study of the soil, and indicates the directions in which the most valuable results must be sought, previously discussing fairly fully the work which has already been done. He shows himself to be possessed of an exceedingly critical spirit, and, in fact, the whole tenour of the book may be described as more destructive than constructive. His main contention is that the lack of agreement between practice and theory and the failure to arrive at other than empirical results is to be ascribed to the tendency of investigators to regard the problem of the soil from a static point of view, when as a matter of fact it is essentially dynamic, and that what is wanted is a thorough and systematic investigation of the properties of the soil solution in relation to the production of crops. For its survey of the recent literature of the chemistry of the soil the book has a very real value, and the author's comments and criticisms are in all cases cogent and to the point, and should prove stimulating and suggestive for future research.

Announcement.—Messrs. Ozonair, Ltd., 96, Victoria Street, Westminster, S.W., advise us that in consequence of the very considerable extension of their business they have, as announced in our last issue, appointed Mr. R. Borlase Matthews, Wh.Ex., M.I.E.E., to the position of Manager. Mr. Edward L. Joseph, Managing Director, will still continue to give the same personal attention to the business.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 6, August 7, 1911.

Photolysis of Alcohols, Acid Anhydrides, Ether Oxides, and Ether Salts by Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—When alcohols are exposed to ultra-violet rays they yield large quantities of hydrogen with formation of aldehydes. Ether oxides give less hydrogen and more hydrocarbons than the alcohols, while acid anhydrides yield no hydrogen and less carbon dioxide than the corresponding acids. Carbon monoxide is the chief product obtained with ether salts.

Synthesis of Berberin.—Amé Pictet and Alphonse Gams.—The authors have synthesised tetrahydroberberin by the following reactions:—1. Condensation of homopiperonylamine with homoveratric chloride. 2. Dehydration of the product by means of phosphoric anhydride. 3. Reduction of the base thus obtained with tin and hydrochloric acid. 4. Treatment of the product, veratrylnorhydrohydrastin, dissolved in hydrochloric acid, with methylal at the temperature of the water-bath. The synthesis of tetrahydroberberin includes that of berberin, the first of these bases having already been converted into the second by the action of oxidising agents.

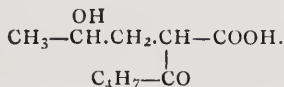
Dithiocamphocarbonic Acid.—L. Tchougæff and G. Pigoulewsky.—The action of carbon disulphide on the sodium derivative of camphor gives dithiocamphocarbonic

acid, $\text{C}_8\text{H}_{14}\begin{matrix} \text{CO} \\ | \\ \text{CH}-\text{CS}-\text{CH} \end{matrix}$, which, on saponification, yields camphocarbonic acid. Dithiocamphocarbonic acid is a yellow oily liquid which is stable at the ordinary temperature, but decomposes when heated, giving camphor and carbon disulphide. The alkaline dithiocamphocarbonates are very soluble in water, giving precipitates and characteristic colourations with most of the salts of the heavy metals. The copper salt is totally different from the cuprous xanthogenates.

Constitution of Divalolactone.—S. Losanitch.—The action of methyl magnesium iodide on dimethyldehydrodivalolactone shows that divalolactone contains a ketonic group. Since, also, it readily regenerates divalolactonic acid its formula must be—



or—



Preparation of α -Naphthalenic Ketones by Friedel and Crafts' Reaction.—E. Caille.—In the ordinary way the application of Friedel and Crafts' reaction in the preparation of the naphthalenic ketones gives a mixture of the α - and β -isomers. If, however, the temperature is kept low only the α -isomer is obtained. It is also advantageous to use carbon disulphide as a solvent.

No. 7, August 14, 1911

Influence of various Physical Conditions on the Ultra-violet Radiation of Quartz Mercury Lamps.—Victor Henri.—The tension of different lamps is not the same, but exhibits small variations which depend probably

upon the degree of evacuation and upon small differences in their dimensions. The ultra-violet radiation of the lamps also differs.

Analysis of Monazite Sands.—G. Chesneau.—2.5 grms. of the finely powdered specimen were fused for an hour at a bright red heat with 15 grms. of KNaCO_3 , and taken up with water containing 1 per cent of soda. The insoluble residue was filtered off, washed with cold water, and treated with 5 per cent HCl. The residue was subjected to the same treatment. Thus three preparations were obtained:—1. The hydrochloric acid solution A, containing the rare earths with TiO_2 , ZrO_2 , Fe, &c. 2. An insoluble residue B, containing traces of silica and lime. 3. An alkaline solution C, which contained Al_2O_3 , SiO_2 , and all the phosphoric acid of the mineral. B and C were analysed by the usual methods. A was diluted, treated with crystallised oxalic acid, and allowed to stand for two days. The liquid then contained the TiO_2 , ZrO_2 , Fe, &c., which were determined in the usual way, and the precipitate consisted of the oxalates of the rare earths. It was heated nearly to 500° , and the oxides were taken up with concentrated HNO_3 , and perhydrol was added. After evaporation to dryness the thorium was determined in the aqueous solution by Wyruboff and Verneuil's method of double precipitation with pure H_2O_2 . The filtrate was made up to 500 cc., and all the rare earths precipitated with ammonia. The cerium was determined volumetrically in 100 cc. by Job's method, and the yttrium earths by the potassium double sulphate method. The oxides of lanthanum and the two didymiums were determined by difference. The following are the results obtained with a specimen of monazite sand from Madagascar:—

Thorium oxide	5.5
Cerium oxide	22.6
Lanthanum and didymium oxides ..	25.0
Yttrium earths	0.8
Zirconium oxide	1.6
Ferric oxide	3.7
Aluminium oxide	0.8
Manganese	Traces
Magnesium oxide	0.4
Lime	0.5
Phosphoric acid	23.5
Silica	8.8
Titanic acid	6.7
Loss on ignition	0.4

100.3

No. 8, August 21, 1911.

Glucoside in Leaves of Pear Trees.—Em. Bourquelot and A. Fichtenholz.—The authors have detected the presence of arbutin, $\text{C}_6\text{H}_4(\text{OH})(\text{OC}_6\text{H}_4\text{O}_5)$, in the leaves of four different varieties of pear. The same glucoside is present in the extremities and bark of the branches, and in the skin of the root, but is almost entirely absent in the root itself. The leaves of the apple do not contain any glucoside hydrolysable by emulsion.

No. 9, August 28, 1911, and No. 10, September 4, 1911.

These numbers contain no chemical matter.

No. 11, September 11, 1911.

Employment of Combustion under Pressure to Determine Carbon in Steels.—P. Mahler and E. Goutal.—The sample of steel is placed in a capsule made of a refractory earth, free from calcium carbonate, and is ignited electrically in a bomb of 1 litre capacity containing oxygen at a suitable pressure. The carbon dioxide formed is absorbed by baryta water, and titrated with oxalic acid. This method of determining carbon is specially applicable to steels containing only small amounts of it.

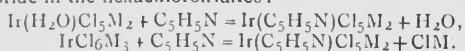
Bulletin de la Société Chimique de France.
Vol. ix.-x., No. 14, 1911.

Separation and Determination of Ammonia and Pyridine.—M. Delépine and R. Sornet.—The liquid containing the ammonia and pyridine is acidified with a little hydrochloric acid, and the following solutions are added :—

50—100 cc. of HgCl ₂	30 grms. per litre
30 " Na ₂ CO ₃	200 " "
5—10 " NaOH	400 " "

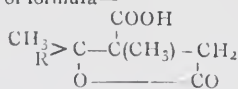
After being made up to a known volume, eight- or nine-tenths of the liquid is filtered off, diluted, and distilled into hydrochloric acid. Slight excess of chloride of gold or platinum is added, and the pyridine is weighed as chloraurate or chloroplatinate. The mercuric precipitate containing the ammonia is washed with alkali. Fifty cc. of a solution of sodium hyposulphite (200 grms. per litre) are added to the precipitate, and it is distilled in a current of steam, the ammonia being received in an excess of HCl. The ammoniacal solution is then evaporated, and the NH₄Cl weighed.

Pyridino-pentachloroiridites.—M. Delépine.—The pyridino-pentachloroiridites can be prepared by replacing a molecule of water in the aquopentachloroiridites by pyridine, or by replacing similarly a molecule of alkaline chloride in the hexachloroiridites :—



The alkaline salts can easily be prepared thus, but the yields are not good unless certain precautions are observed. Only a very few other pyridino-pentachloroiridites can be obtained by double decomposition with the alkaline salts. The pyridino-pentachloroiridites with chlorine, nitric acid, or aqua regia lose an atom of metal, giving a new series of compounds pyridino-pentachloroiridates, Ir(C₅H₅N)Cl₅M. The pyridine and iridium are very strongly bound to one another in the iridites, and the alkaline salts are not affected by dilute acids even at 100°.

Action of Organo-magnesium Compounds on Methyl Acetylpyrotartrate.—Ph. Barbier and R. Locquin.—The action of magnesium isobutylbromide on methyl acetylpyrotartrate gives an ether of an acid alcohol which, on saponification, yields methyl isobutyl, ketone, and pyrotartaric acid, but no trace of the disubstituted paraconic acid, the formation of which was to be expected on theoretical grounds. Similar results are obtained with magnesium phenyl bromide. Thus the disubstituted paraconic acids of formula—



are stable only in the form of ether.

New Synthesis of Methyl Ketones.—Ph. Barbier and R. Locquin.—When any organo-magnesium derivative R—Mg—X acts on a disubstituted derivative of acetylacetic

CH₃—CO—C—CO₂R¹,
ether of the type



, a methyl ketone,

CH₃—CO—R, and the acid, R¹ > CH—CO₂H, are formed, while with a substituted derivative of the type CH₃—CO—C—CO₂R³



a ketone, CH₃—CO—CH₂—CH < R¹,
is obtained. By means of these reactions various methyl ketones can be obtained which are difficult to prepare otherwise.

Action of Acid Chlorides and Anhydrides on Monosodium Benzyl Cyanide.—F. Bodroux.—Monosodium benzyl cyanide reacts violently with acetyl chloride, giving 2-phenyl 3-butanone 1-nitrite. Probably acetamide is formed as an intermediate product, and is transformed into its sodium derivative. A similar reaction occurs with acetic anhydride, but the yield is very small. Benzoyl

chloride, on the other hand, gives excellent results, the product being 1-2-diphenyl 1-propanone 3-nitrite.

Hydrogenation in presence of Divided Palladium.—P. Breteau.—When phenanthrene is hydrogenated in presence of palladium sponge, the product is a mixture of the tetra- and octo-hydrides. No trace of the dihydride is formed. The hydrogenating action of palladium sponge is not due to the formation of a hydride, but to the power palladium possesses of retaining large volumes of the gas (589 vol.), which thus becomes as active as the compressed gas.

Catalysis of Borneol and Catalytic Hydrogenation of Camphor.—J. Aloy and V. Brustier.—Borneol vapour, when passed over divided copper at 230—350°, is transformed into camphor. At 300° the theoretical yield is obtained. At 420—430° and upwards, terpenes are formed. Sabatier and Senderens' method of hydrogenation is not applicable to camphor, but it enables camphor oxime to be converted into amines, the chief product being the secondary amine.

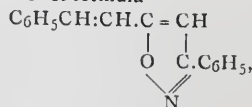
Preparation of Oxy-indazols from Unsubstituted Azoic or Hydrazoic Acids.—P. Freundler.—By the action of phosphorus pentachloride the azoic or hydrazoic acids are transformed into the chlorinated hydrazoic acids, which lose a molecule of water, to give the corresponding oxy-indazols. The yields are very variable.

Benzene-azoxy-o-benzoic Acid.—P. Freundler.—This compound, which has not previously been prepared, may be obtained by gently heating phenylhydroxylamine with o-nitrosobenzoic acid in an alcoholic solution. When the nitroso acid has disappeared the alcohol is distilled off, the residue taken up with ether, and sodium carbonate solution is added. The alkaline liquid is then acidified with dilute HCl, the resinous precipitate is again taken up with ether, and the ethereal solution is shaken with baryta water, which dissolves the benzene azoxybenzoic acid. The excess of baryta is eliminated by means of a current of CO₂, and on acidification the pure crystalline acid is obtained in the form of yellowish crystals fusing at 110—111°.

Atti della Reale Accademia dei Lincei.
Vol. xx., (II.), No. 1, 1911.

Derivatives of Oxyhydroquinone.—G. Bargellini and Ermanno Martegiani.—The trimethyl ether of oxyhydroquinone reacts with propionylchloride, giving 4.5-dimethoxy-2-oxo-propionophenone. From the dimethyl ether acetyl and benzoyl benzoyl derivatives can be prepared. Also 2.4.5-trimethoxy-propionophenone is obtained when the dimethyl ether is treated with sodium hydrate, and a slight excess of dimethyl sulphate is added. The trimethyl compound with amyl nitrite gives isonitrosotrimethoxy-propionophenone.

Action of Hydroxylamine on Ketones of the Type R.CH:CH.CH:CH.CO.C₆H₅.—R. Ciusa and A. Terni.—Two molecules of hydroxylamine combine with one of cinnamylidene-acetophenone to give a hydroxylamine oxime, which, on oxidation yields benzoic acid and a substance of empirical formula C₁₇H₁₅ON. The latter is a styrylphenylisoxazol of formula—



The hydroxylamine oxime with nitrous acid gives a substance of formula C₁₇H₁₅ON.

MEETINGS FOR THE WEEK.

FRIDAY, 27th.—Physical, 5. "Further Observations on the After-glow of Electric Discharge and Kindred Phenomena," by Hon. R. J. Strutt. "Homogeneous Fluorescent X-radiation of a Second Series," by C. G. Barkla and J. Nicol.

THE CHEMICAL NEWS.

VOL. CIV., No. 2709.

THE INFLUENCE OF CONSTITUTION ON THE MOLECULAR VOLUMES OF ORGANIC COMPOUNDS AT THE BOILING-POINT.*

By GERVAISE LE BAS, B.Sc.

(Concluded from p. 189).

Application of Molecular Volumes to the Investigation of Ring Compounds.

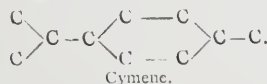
In the following calculations N represents the number of groups in the ring, and *n* the number of carbon atoms:—

Compound 1: Formula $C_{10}H_{14}$.

$$M.V. = 184.9 \quad \Sigma A.V. = 199.8 \quad \Delta = -14.9$$

$$N = \frac{14.9}{2.45} = 6 \quad n = 10 \quad n > N$$

The substance contains a single six-membered ring. There are $10 - 6 = 4$ carbon atoms outside the nucleus.



Compound 2: Formula $C_{10}H_{16}$.

$$M.V. = 147.2 \quad \Sigma A.V. = 177.6 \quad \Delta = -30.4$$

$$N = \frac{30.4}{2.45} = 12 \quad n = 10 \quad n < N$$

The substance contains a condensed double ring with $12 - 10 = 2$ atoms common to the two groups.



Compound 3: Formula $C_{14}H_{10}$.

$$M.V. = 195.5 \quad \Sigma A.V. = 244.2 \quad \Delta = -48.7$$

$$N = \frac{48.7}{2.45} = 20 \quad n = 14 \quad n < N$$

The substance contains a complex and condensed ring system of 20 groups in all, but consisting of only 14 C atoms. There must therefore be a considerable number of C atoms common to the rings.

The following formula answers to the conditions:—



This is the formula of anthracene.

Camphor, $C_{10}H_{16}O$, and borneol, $C_{10}H_{18}O$, which possess bridged rings, are subject to contractions of 30.6 and 31.5 respectively. Since they contain a bridged ring the two parts of which contain five members or ten in all, the contractions should be about 24. This leaves a contraction of 6 or 7 units to be accounted for. The two methyl groups might contribute to the contraction and so explain the difference, but I think there is a better explanation. If we remember the tetrahedral properties of carbon we find the accompanying formula for camphor possible. (See p. 201).

Besides the double five membered ring, there is now seen to be an incomplete four membered ring which would naturally increase the contraction. Speaking generally, the above solid arrangement of the C atoms is more compact than in the plane formula. On examining chemical literature I find that in 1906 Foster (*Trans. Chem. Soc.*, 472, p. 268) considered a formula for bromnitrocamphane which was similar to the above. It would not be remarkable if all these compounds possessed such a formula.

Finally, as an example of the great use of molecular volumes in the elucidation of the constitution of compounds, the various compounds which are formed when isoprene polymerises may be briefly studied.

Isoprene, C_5H_8 —M.V. 193.9; W.S. $28 \times 3.7 = 103.6$ Conti.
This is an open chain di olefin.

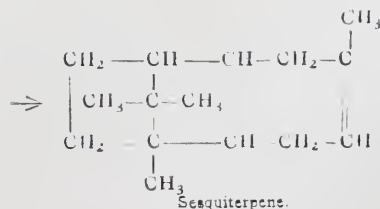
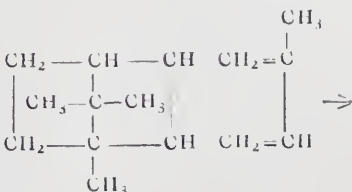
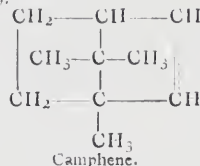
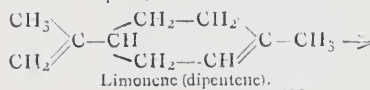
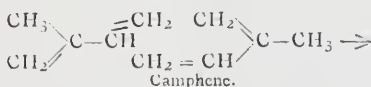
Dipentene, $C_{10}H_{16}$ —M.V. 190.5; $\Sigma A.V. 2 \times 103.9 = 207.8$ 17.3
This corresponds with a single six-membered ring.

Camphene, $C_{10}H_{16}$ —M.V. 177.9; $\Sigma A.V. 207.8$ 29.9
There is a bridging of the ring. Moreover, some sort of bridged ring must be intermediate between dipentene and the sesquiterpenes.

Sesquiterpenes, $C_{15}H_{24}$ —M.V. 266.6; $\Sigma A.V. 3 \times 103.9 = 311.7$ 15.1

Diaterpenes, $C_{20}H_{30}$ —M.V. 355.2; $\Sigma A.V. 4 \times 103.9 = 415.6$ 60.4

It is remarkable that the four stages increase by 15 units approximately. There must in consequence be three six-membered or analogous rings in the sesquiterpenes, and four six-membered or analogous rings in the diaterpenes. These facts refer to the typical members only, for their constitutions differ considerably. It follows that a bridged ring must be the foundation of the sesquiterpenes, the diaterpenes, and thus probably of indiarubber. For purposes of illustration we will suppose it to be camphene, since I believe this hydrocarbon together with pinene is found among the decomposition products of indiarubber. The stages thus are—



* A Paper read before the British Association Section B, Portsmouth Meeting, 1911.

TABLE I.—*The Effect of Complexity on Molecular Volumes in a Typical Homologous Series at the Boiling-point.*

Compound.	W.	M.V.	V/W.	Δ .	CH ₂ .
Octyl octylate, C ₇ H ₁₅ COOC ₈ H ₁₇	101	404.3	4.002	0.034	24.03
Heptyl octylate, C ₇ H ₁₅ COOC ₇ H ₁₅	95	377.0	3.968	0.033	23.80
Heptyl heptylate, C ₆ H ₁₃ COOC ₇ H ₁₅	89	350.2	3.935	0.033	23.61
Heptyl caproate, C ₅ H ₁₁ COOC ₇ H ₁₅	83	323.9	3.902	0.037	23.41
Heptyl valerate, C ₄ H ₉ COOC ₇ H ₁₅	77	297.4	3.865	0.034	23.19
Hexyl valerate, C ₄ H ₉ COOC ₆ H ₁₃	71	272.0	3.831	0.030	22.98
Heptyl propionate, C ₂ H ₅ COOC ₇ H ₁₅	65	247.1	3.801	0.033	22.80
Amyl butyrate, C ₃ H ₇ COOC ₅ H ₁₁	59	222.3	3.768	0.036	22.60
Propyl valerate, C ₄ H ₉ COOC ₃ H ₇	53	197.8	3.732	0.024	22.39
Ethyl valerate, C ₄ H ₉ COOC ₂ H ₅	47	174.3	3.708	0.035	22.25
Butyl acetate, CH ₃ COOC ₄ H ₉	41	150.6	3.673	—	22.08
Propyl acetate, CH ₃ COOC ₃ H ₇	35	128.4	3.668	—	22.00
Propyl formate, H.COOC ₃ H ₇	29	106.2	3.662	—	21.97
Ethyl formate, H.COOC ₂ H ₅	23	84.6	3.678	—	22.07
Methyl formate, H.COOC ₂ H ₅	17	62.7	3.688	—	22.13
Mean value.				0.033	

TABLE II.—*Constitutive Effect in the Polysubstituted Paraffin Derivatives.*

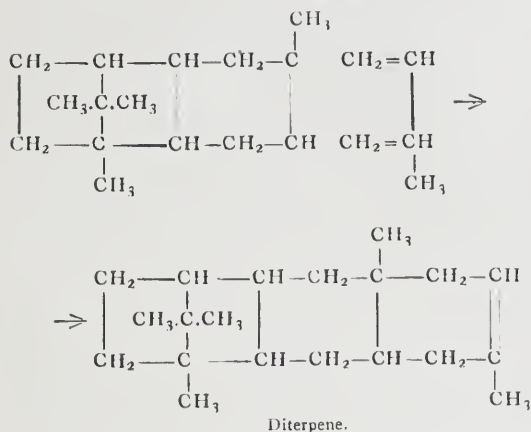
Compound.	W.	M.V.	Σ A.V.	Δ .
X ₁ . Allyl chloride, C ₃ H ₅ Cl	23	84.4	84.6	—
Propyl chloride, C ₃ H ₇ Cl	25	91.7	92.0	—
Propyl bromide, C ₃ H ₇ Br	—	97.3	98.0	—
Propyl iodide, C ₃ H ₇ I	29	107.3	106.7	—
X ₂ . Methylene chloride, CH ₂ Cl ₂	18	65.3	66.2	—
Ethylidene chloride, CH ₃ CHCl ₂	24	88.9	88.3	—
Benzylidene chloride, C ₆ H ₅ CHCl ₂	—	151.7	155.3	—
Ethylene chloride, CH ₂ Cl.CH ₂ Cl	24	85.3	88.3	-3.0
Ethylene bromide, CH ₂ Br.CH ₂ Br	—	97.0	100.0	-3.0
Ethylene chloriodide, CH ₂ ClCH ₂ I	28	101.0	103.4	-2.4
Propylene dibromide, CH ₃ .CHBr.CH ₂ Br	—	119.2	122.4	-3.2
Propylene dichloride, CH ₃ CHClCH ₂ Cl	30	107.9	110.4	-2.5
Propylene glycol, CH ₃ CH(OH).CH ₂ (OH)	24	85.4	88.3	-2.9
Trimethylene dibromide, CH ₂ Br.CH ₂ CH ₂ Br	—	118.1	122.4	-4.3
Trimethylene glycol, CH ₂ OH.CH ₂ CH ₂ OH	24	84.2	88.3	-4.1
X ₃ . Carbonyl chloride, COCl ₂	19	70.0	70.3	—
Acetyl chloride, CH ₃ COCl	20	74.2	74.0	—
Chloroform, CHCl ₃	23	84.8	85.1	—
Bromoform, CHBr ₃	—	103.8	103.0	—
Trichlorethane, CH ₃ CCl ₃	30	—	—	—
Chlorethylene dichloride, CH ₂ ClCHCl ₂	29	103.1	106.7	-3.6
X ₄ . Tetrachlormethane, CCl ₄	28	104.0	103.6	—
Bromotrichlormethane, CCl ₃ Br	—	108.8	109.1	—
Tetrachlorethylene, CCl ₂ .CCl ₂	32	114.7	117.7	-3.0
X ₅ . Pentachlorethane, C ₂ HCl ₅	39	139.3	143.5	-4.2
Trichloroacetyl chloride, C ₂ Cl ₄ O	35	125.9	128.9	-3.0

TABLE III.—*Evidence of a Volume Disturbance in Monosubstituted Benzene Compounds.*

Compound.	M.V.	Σ A.V.—R.	Δ .	Au.	Compound.	M.V.	Σ A.V.—R.	Δ .	Au.
C ₆ H ₅ OH	101.8	103.4	-1.6	Pt	C ₆ H ₄ NCH ₃ (picolene)	111.5	110.8	—	Th
C ₆ H ₅ OC ₂ H ₅	125.2	125.6	—	"	C ₆ H ₄ CH ₃ NH ₂	128.9	133.0	-4.1	"
C ₆ H ₅ OC ₂ H ₅	148.8	148.8	—	"	N(C ₂ H ₅) ₃	222.1	222.0	—	Z
C ₆ H ₄ CH ₃ .OH	123.7	125.6	-1.9	"	C ₆ H ₅ N(C ₂ H ₅) ₂	243.5	244.0	—	"
C ₆ H ₅ CH ₂ OH	123.7	125.6	-1.9	"	C ₆ H ₅ NO ₂	122.1	124.8	-2.7	Nb
C ₆ H ₄ CH ₃ OC ₂ H ₅	148.0	148.8	—	"	C ₆ H ₄ CH ₃ NO ₂	144.1	146.3	-2.2	"
C ₆ H ₅ COOH	123.7	129.3	-5.6	Kp	C ₆ H ₅ CN	121.6	123.0	-1.4	K
C ₆ H ₅ COOC ₂ H ₅	150.3	151.5	-1.2	"	C ₆ H ₅ Cl	114.6	115.0	—	S
C ₆ H ₅ COOC ₂ H ₅	174.2	173.7	—	"	C ₆ H ₅ Br	120.0	120.0	—	"
C ₆ H ₅ OH.COOC ₂ H ₅	157.0	158.9	-1.9	"	C ₆ H ₅ I	130.7	129.8	—	"
C ₆ H ₅ CH:CHCOOH	162.3	166.3	-4.0	Wg	C ₆ H ₅ CHO	118.4	118.2	—	"
C ₆ H ₅ CH:CH.COOC ₂ H ₅	188.6	188.5	—	"	C ₆ H ₅ CHCl ₂	154.7	155.2	—	"
C ₆ H ₅ CH ₂ .CH ₂ COOH	170.9	173.7	-2.8	"	C ₆ H ₅ CH ₂ Cl	133.8	135.7	-1.9	"
C ₆ H ₅ CH ₂ .CH ₂ COOC ₂ H ₅	196.0	195.9	—	"	C ₆ H ₅ COCl	137.8	140.9	-3.1	"
C ₆ H ₅ NH ₂	106.4	110.8	-4.4	Th					

TABLE IV.—Comparison of the Volumes of the Isomers of Benzene Derivatives.

Compound	Groups.	<i>o.</i>	<i>m.</i>	<i>p.</i>	Δ .
Xylene, C_8H_{10}	$X_1 = CH_3$ $X_2 = CH_3$	138.2	140.0	140.4	-2.2
Methyl propyl benzene, $C_{10}H_{14}$	$= CH_3$ $= C_3H_7$	—	187.6	187.6	—
Cresol, C_7H_8O	$= CH_3$ $= OH$	121.8	123.5	123.8	-2.0
Cresyl meth. oxide, $C_8H_{10}O$	$= CH_3$ $= OCH_3$	146.4	147.7	148.0	-1.6
Cresyl ethyl oxide, $C_9H_{12}O$	$= CH_3$ $= OC_2H_5$	171.2	172.4	172.4	-1.2
Cresyl propyl oxide, $C_{10}H_{14}O$	$= CH_3$ $= OC_3H_7$	195.4	196.7	196.7	-1.3
Cresyl butyl oxide, $C_{10}H_{14}O$	$= CH_3$ $= OC_4H_9$	218.8	220.9	221.3	-2.5
Toluidine, C_7H_9N	$= CH_3$ $= NO_2$	126.9	128.3	128.9	-2.0
Nitrotoluidine, $C_7H_7NO_2$	$= CH_3$ $= NH_2$	142.6	144.3	145.2	-2.6



There is always a terminal olefine linking, so that the polymerisation can go on indefinitely till compounds of the order of complexity of indiarubber are reached.

Since the polymerisation, and indeed the decomposition, takes place with great facility, and, moreover, the steps are probably similar, it is probable that a double chain series of compounds is formed rather than a complex ring system which spreads in all directions. According to the evidence of molecular volumes the $\begin{smallmatrix} CH_3 \\ CH_2 \end{smallmatrix} \geq C -$ group of isoprene does not persist, and thus a bridged ring is the foundation of the typical polyterpenes.

It should be mentioned that the sesquiterpenes and the diterpenes probably possess different varieties of structure. The above results are typical.

The molecular refractions of most of the compounds show the presence of only one olefine linking, as is necessitated by the above schemes.

It should be stated that a combined use of molecular volumes at the boiling-point and molecular refractions constitutes an excellent means of elucidating the chemical constitution of compounds, the first explaining the ring structure, the second the number of olefine linkings.

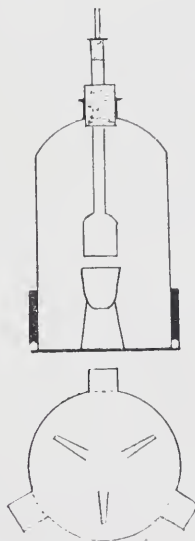
A SIMPLIFIED COMBUSTION CALORIMETER.

By R. WRIGHT.

THIS calorimeter—which is a modification of the William Thomson and Darling instruments—has been devised in order to provide a simple apparatus suitable for students' use.

It consists of a glass bell-jar carrying on its flange a lead weight heavy enough to sink the jar when filled with oxygen. The weight is either made by wrapping sheet lead round the base of the jar, or preferably by preparing a ring shaped casting, which will slip over the jar and be held in position by the flange. The fuel is contained in a nickel crucible ($1\frac{1}{2}$ in. diameter) supported on a small tripod, which is part of the brass base plate.

The base plate is cut from heavy sheet brass, and is of the form shown, the crucible tripod is made by bending the narrow inner tongues at right-angles to the base-plate



while the broad tongues at the edge of the plate serve to clamp it to the base of the jar.

The oxygen for the combustion is led through a tube of Jena glass, which should slide fairly easily in the cork fitted to the neck of the bell jar; the tube is enlarged at its lower end, while at the upper it is fitted with a cork and delivery tube for the oxygen.

The device recommended by Kershaw ("Fuel, Water, and Gas Analysis") of fitting the outside of the jar with a ring of brass-wire gauze so that it projects at right angles to the sides, not only serves to break up the bubbles of escaping gas but also holds the jar in position in the beaker used as calorimeter.

The weighed fuel ($\frac{1}{4}$ grm.) being placed in the crucible, the latter is fixed in the tripod, and the base plate clamped

in position; the air in the jar is now replaced by oxygen, and the fuel ignited by removing the cork from the delivery tube, and dropping in a small piece of glowing charcoal or red-hot copper wire; the heat evolved by this addition can either be calculated, or by using a constant weight of charcoal may be made part of the factor of the instrument.

The apparatus is at once connected with the oxygen supply, and lowered into the water contained in the beaker. The oxygen tube, which is raised at first, is lowered as the combustion proceeds until it is quite close to the glowing fuel; before admitting the water to the inside of the jar at the end of the determination it is advisable to raise the delivery tube so that it is not cracked by contact with the cold water; this danger can, of course, be avoided by having the tube made of brass.

The factor for the instrument which corrects for errors due to its thermal capacity, radiation, &c., is found by the usual method of burning a substance of known calorific value, such as cellulose, carbon, or naphthalene.

In conclusion, it is to be noted that the calorimeter has the defects common to all of this type. Very volatile coals must be mixed with some non-inflammable substance to prevent loss by too quick combustion, while anthracite should be mixed with a bituminous coal of known calorific value. Also the time taken by the combustion (five to ten minutes) is a source of error, unless care is taken that all determinations occupy equal times when the error becomes part of the factor of the instrument.

The Sir Donald Currie Laboratories,
The Queen's University, Belfast,
October 11, 1911.

A COLORIMETRIC METHOD FOR VANADIUM IN IRON AND STEEL.*

By CHAS. R. McCABE, Engineer of Tests, the Lima Locomotive and Machine Co., Lima, O.

(Concluded from p. 196).

Presence of Tungsten.

When tungsten is present in a vanadium steel the filtrate from the tungsten determination is used for the vanadium determination. An important fact to be remembered in this case is that the evaporation to dryness in the tungsten determination has reduced a portion of the vanadium. It is therefore necessary to re-oxidise it during the evaporation of the filtrate preceding the ether separation of iron. To the filtrate add 5 cc. of nitric acid (1.2 sp. gr.), and proceed according to the presence or absence of chromium. Avoid the use of sulphuric acid in the tungsten determination.

Presence of Titanium.

Although hydrogen peroxide gives a yellow colour with titanium, nevertheless presence of titanium does not interfere with the vanadium determination. This is due to the fact that hydrofluoric acid in the amount prescribed destroys the colour due to titanium. This is true for any amount of titanium apt to occur in iron or steel. The colour of vanadium with hydrogen peroxide, however, is slightly modified in presence of titanium. Comparison by artificial light is advisable when titanium is present. The dissimilar character of the colour then vanishes, and the eye perceives only their relative depths. The error, if any, due to titanium is slight.

Presence of Molybdenum.

Molybdenum, like titanium, gives a yellow colour in acid solution with hydrogen peroxide. However, the properties of molybdenum are such that when present in a vanadium steel it does not appear in the solution in which the

vanadium colour is produced, the bulk being removed in the ethereal separation with iron, and the balance in the ammoniacal filtrates with nickel and chromium.

Pig Iron.

The application of this method to pig-irons is obvious. It is only necessary to remove the insoluble in any convenient manner, avoiding the use of sulphuric acid. As in tungsten steels, the reducing action on vanadium of a complete evaporation of the acid solution must not be forgotten, and an oxidiser, preferably nitric acid, added to the hydrochloric acid solution previous to the ether separation of iron.

There are certain limitations to this method which must be understood in order to apply it successfully. A cardinal rule is to treat standard and test exactly alike in making the comparison. The vanadium colour with hydrogen peroxide is sensitive, and neglect of this precaution will lead to erroneous results. Another feature is the limited capacity of ferric hydrate to occlude vanadium. This property of ferric hydrate is such that with a 2-grm. sample of vanadium steel, the amount of iron, one-tenth grm., used in the acid solution preceding the ammonia precipitation occludes all the vanadium without appreciable loss when the percentage is under 0.20. Above 0.20 per cent and under 0.30 per cent the loss may be neglected in ordinary routine analysis. But above 0.30 per cent the loss rapidly increases, so that it is necessary to take a smaller sample for analysis. A safe working rule is to take such a sample that the contained vanadium is not in excess of 6 mgrms. When less than 2 grms. of sample is taken for analysis the amount of iron necessary in the acid solution following the ether separation, namely, one-tenth grm., may be obtained by taking more of the ethereal solution. Or some of the ferric chloride solution may be added.

An important precaution is to avoid any step in the analysis which tends to reduce vanadium. A small amount of reduced vanadium is reoxidised by hydrogen peroxide itself after a lapse of about ten minutes with a simultaneous development of colour, but large amounts are only imperfectly reoxidised by the limited amount of hydrogen peroxide.

The question of the reliability of this method is one which cannot be judged by a comparison of its results with those of older methods. Rather, we must pass judgment by a careful analysis of the method itself, the principles on which it depends, and its sources of error. It may be said, however, that the Bureau of Standards Sample No. 24, containing 0.15 per cent vanadium, shows an exact check. It also shows the correct result when nickel, chromium, titanium, and molybdenum are added to the hydrochloric acid solution preceding the ether separation. In view of the care exercised in the analysis of this sample, such a result appears not without value. With certain analysed samples submitted by interested parties for confirmation the method showed somewhat high results, amounting to 0.05 per cent in one instance. Others showed a very satisfactory check. To interpret such evidence, we are obliged to examine our method and judge independently of its merits. It is not unfair to consider that every factor which influences the colour of the vanadium with hydrogen peroxide is under control; that the property of ferric hydrate of occluding vanadium quantitatively is easily demonstrable; and that if there is any source of serious error it remains to be discovered. Note must be taken of the anomalous circumstance that the method often shows high results compared with older methods. Slightly low results might reasonably be expected, since the power of ferric hydrate to occlude vanadium, while satisfactory for our purpose, is not absolutely perfect. This consideration directs suspicion to the older method when the two show discordant results. But the evidence which appeals most strongly to reason is that obtained by the analysis of artificial mixtures of vanadium solutions with solutions of plain and special alloy steels. Such mixtures have always shown

* From the *Chemical Engineer*, xiii., No. 6.

the true vanadium content, within very reasonable limits. The recovery of all the vanadium present in the hydrochloric acid solution thus being an established fact, the correctness of the vanadium standard may be confirmed, and the chain of evidence is complete.

It is perhaps too much to claim that this method is universally applicable to all irons and steels. Reference has been made to the influence of elements occurring in vanadium steels on the colour. It must be understood that these observations refer only to the quantities of these elements commonly found in vanadium steels. When present in abnormally large quantities, the question of the availability of the method must rest on the judgment of the operator. But it may be affirmed without reserve, that material to which this method is inapplicable is of rare occurrence.

The writer acknowledges his obligations to the following parties for materials and samples furnished during the experimental work: Geo. L. Norris, of the American Vanadium Co., Pittsburg, Pa.; J. Lloyd Uhler, of the Union Steel Casting Co., Pittsburg, Pa.; C. M. Johnson, of the Crucible Steel Co., Pittsburg, Pa.; and the Primos Chemical Co., Primos, Pa. Credit is also due to Booth, Garret, and Blair for correcting a misstatement relative to the non-interference of molybdenum.

CELLULOSE FROM ACETYLCELLULOSE.

UP to the present, acetylcellulose found application only as a varnish for coating objects where non-inflammability and certain electric properties were required. The main use was for the manufacture of cinematograph films, which did not burn even after ignition. Altogether, it has been impossible to make objects from it more than one-fourth of a millimetre in thickness.

Dr. A. Eichengrün has now discovered (*Zeitschrift für Angewandte Chemie*, 1911, 366) a method of making celluloid of any shape, colour, and thickness, using acetyl cellulose instead of nitrocellulose. In this manner he has produced an incombustible substitute for celluloid which he calls "Cellon." His invention seems to be laid down in his French Patent 412,797 of January 20, 1910, and British Patent 1441 of January 19, 1910, the essence of which is:—

"Certain types of cellulose acetate, notably those which are soluble in acetone, are soluble on heating, in mixtures of liquids, e.g., methyl alcohol and benzene, neither of which have any solvent action alone. On cooling these solutions, the ester may either remain in solution or separate out in the form of long felted filaments. The separation may be prevented by adding to the solution any of the ordinary solvents of cellulose acetate, in which it is soluble in the cold, e.g., glacial acetic acid, acetone, &c., in which case the solution remains liquid or becomes syrupy on cooling. Or else, there may be added a substance having an influence analogous to that of camphor in nitrocellulose, in which case the solution sets to a continuous mass on cooling. Suitable bodies are methyl acetanilide, ethyltoluenesulphonate, trichloraniline, &c. If a very concentrated mass be desired, the cellulose acetate may be dissolved in alcohol and benzene, freed from impurities by filtration, and allowed to deposit by cooling; the liquid is then poured off and the precipitated cellulose acetate worked up with a camphor substitute. One of the numerous examples of the process runs as follows:—1 kilo. of cellulose acetate is dissolved in 2 kilos. of methyl alcohol and 1 kilo. of toluene at 80° C.; 150 grms. of methylacetanilide are added to the solution and 100 grms. of epichlorhydrin. The liquid is filtered hot, and on cooling sets to a solid mass, which may be sliced, moulded, or pressed through orifices. In various ways plastic masses having all the technical properties of celluloid may be prepared."—*Journal of Industrial and Engineering Chemistry*, iii., No. 6.

THE FRACTIONATION OF THE YTTRIUM EARTHS BY MEANS OF THE SUCCINATES.

By R. C. BENNER.

DURING the past decade material contributions have been made to the study of the yttrium group of the rare earths. Among these it has been shown by Lenher that, through the agency of the succinates, considerable rapidity can be arrived at in the process of separating various mixtures of these earths. The succinates of the yttrium group are finely divided crystalline precipitates, which are best formed by the addition of a solution of neutral ammonium or sodium succinate to a neutral nitrate solution of the yttrium earths. This precipitate is of especial interest because the time of formation is so greatly delayed that it is possible for equilibrium to become more readily established. Under these conditions the separation is more sharply performed than if precipitation took place instantaneously.

In order to test the applicability of the succinates as reagents in the yttrium group, the yttrium earths were extracted from a number of rare earth minerals of widely differing character and the separation studied in some detail.

Samarските.

The yttrium earths were extracted from samarskite and studied in considerable more detail than previously reported (*Journ. Am. Chem. Soc.*, xxx., 575). The atomic weight determinations and the study of the absorption spectra were used as a continual control on the process of fractionation. The atomic weight determinations were carried out with sufficient accuracy by means of the oxalate method. The absorption spectra studies were made by means of a Steinheil grating spectroscope, similar to the one described by Dennis (*Journ. Am. Chem. Soc.*, xxiv., 415). The earths having the highest atomic weights were precipitated first, showing that the succinates of the earths having lower atomic weights were the more soluble. In all cases the colour of the oxides and the strength of the absorption spectra varied in the same ratio as did the atomic weights, all of which demonstrated that erbium and the other heavy earths concentrated in the first fractions, while yttrium concentrated in the last. Typical illustrations of this separation were given in the following series of atomic weights:—A, 130, 116, 104; B, 123, 115, 98.5; C, 111, 108, 99.7; D, 104, 97.

Monazite.

In order that the influence of various factors in the succinate method might be verified by experiment, several hundred grms. of the yttrium earths were separated from monazite, the solution being effected in nitric acid in such a manner that the solution formed was neutral to methyl-orange.

A sodium succinate solution was made by adding sodium hydroxide to succinic acid until the solution was neutral to phenolphthalein, after which the strength was determined. An ammonium succinate solution of equal strength was prepared by the addition of ammonia to succinic acid until neutral to litmus. Sixty cc. of the yttrium earth nitrate solution, containing 7.81 grms. of rare earth oxides, were diluted to 1 litre, and fractionated in various ways, so that six fractions were obtained in each case.

Experiment 1.—The effect of fractionation in dilute was compared with the same operation in a strong solution, the strength of the succinate being varied as well as that of the earths.

Experiment 2.—The relative value of sodium succinate as a precipitating agent was compared with that of ammonium succinate.

Experiment 3. The rapid addition of the succinates was compared with the addition of the same reagent drop by drop.

Experiment 4.—The effect of stirring during precipitation was studied.

Experiment 5.—The addition of various substances to the solution, such as sodium or ammonium acetate and nitrate, was studied.

The separation was most satisfactorily made when the precipitating reagent was added drop by drop. Sodium succinate appeared to be slightly superior to ammonium succinate as a precipitating reagent. The separation was apparently not aided by the presence of sodium acetate or nitrate, or by the corresponding ammonium salts.

Behaviour of Sodium Succinate towards Mixtures of the Cerium and Yttrium Groups.

The material chosen for this experiment was a mixture of the monazite earths containing a large portion of the earths of the cerium group. The oxalates of this mixture were ignited to the oxide, dissolved in nitric acid, and evaporated to a syrup. The cerium was reduced to the cerous form by hydrogen peroxide, and the excess destroyed by boiling the solution. The solution containing 61 grms. of these oxides, in form of the neutral nitrates, was diluted to 1 litre, and fractionally precipitated by means of a 10 per cent sodium succinate solution, 100 cc. of the solution being added at one time. The fractions, after being ignited to the oxide, were of a similar dark brown colour, except the last two, which were of a lighter shade. Their atomic weights were as follows:—149·5, 147·0, 147, 150·0, 149·0, 146·0, 143·0, 143·0, 143·0. It was evident that there was very little separation of the elements of lower atomic weight from those of higher. The absorption spectra of these fractions failed to show any difference except in case of the last, in which the didymium lines were fainter, and the oxide had a slightly paler colour than that of the previous fractions.

Xenotime.

Ninety-five grms. of the finely powdered mineral were thrown, in small amounts at a time, into fused hydrogen ammonium sulphate. The greenish mass was extracted with water containing a little hydrochloric acid, and the extraction continued until ammonia no longer gave a precipitate. This was then treated with an excess of potassium sulphate, and the soluble double sulphates precipitated with oxalic acid, and converted to the oxides by ignition. These oxides were converted to the neutral nitrates, and a solution of 6·83 grms. per litre was fractioned with a 2 per cent sodium succinate solution. In this instance the sodium succinate solution was added drop by drop, the solution being kept at a boiling temperature and constantly stirred with a mechanical stirrer. Each fraction was filtered after the addition of 12·5 cc. of the sodium succinate solution, and the treatment repeated on the filtrate, the volume being kept at 1 litre during the experiment. The following different fractions were obtained:—112·5, 109·4, 105·7, 101·6, 98·5. By comparison of the different fractions as to colour of the ignited oxides and the absorption spectra, it was noted that elements of higher atomic weight concentrated in the first fractions, while yttrium accumulated in the mother-liquor. This followed in all respects the yttrium earths from samarskite.

Gadolinite, from Langesundfjord, Norway.

Ninety-five grms. of the finely powdered mineral were treated with aqua regia until the residue was colourless, the solution evaporated to dehydrate the silica, the residue extracted with water, and to the clear solution ammonium oxalate added as long as a precipitate formed. These oxalates were converted to the oxides, dissolved in the least possible amount of hydrochloric acid, treated with an excess of potassium sulphate in the cold, and the soluble double sulphates precipitated by means of oxalic acid. Twenty-five grms. of the oxides were converted to the neutral nitrates, diluted to 1 litre, and fractioned by successive additions of 40 cc. of a 1 per cent solution of sodium succinate. The atomic weights of the fractions obtained were:—113·8, 109·9, 108·0, 107·3, 105·6, 103·2, 98·1, 95·1.

The yttrium earths from this specimen of gadolinite were

in all respects similar to those from xenotime, as far as the behaviour toward sodium succinate was concerned. The colour of the oxides and the absorption spectra were found to be similar to the earths from xenotime, except for the more gradual change in atomic weights, which latter would be expected on account of the greater number of fractions.

Fergusonite, from Gaalenene, Norway.

105 grms. of the finely powdered mineral were fused with 400 grms. of potassium acid sulphate. The fused mass was pulverised, extracted with ice water, and washed with cold water until the washings failed to give a precipitate with ammonia. The solution was treated with ammonia, and the precipitate obtained dissolved in nitric acid, and heated for several days, water being added to replace that lost by evaporation. The precipitated metallic oxides were filtered off, the filtrate neutralised, and the earths precipitated by means of oxalic acid. To the hydrochloric acid solution of the earths potassium sulphate was added, and the soluble double sulphates, when free from didymium, were precipitated with oxalic acid, and converted to the oxides. Ten and eighty-five hundredths grms. of the oxides were changed to the nitrates, the solution made neutral to methyl-orange, and diluted to 1 litre. This solution was fractioned by the addition of 25 cc. portions of a 5 per cent sodium succinate solution, the solution being constantly stirred, and the volume kept constant. Atomic weight and spectroscopic observations were made on the various fractions. The atomic weights were:—115·4, 112·4, 110·5, 102·5.

This series was of more interest than any of the preceding, as the spectroscopic observations showed the mixture to be of a more complex character. The separation, however, appeared to be somewhat sharper in the more rapid disappearance of the number of lines. The oxides were found more varied in colour than was the case with the other minerals.

Euxenite, from Arendal, Norway.

300 grms. of the mineral were treated in a lead dish with hydrofluoric acid until the action ceased. The insoluble fluorides were washed with hydrofluoric acid until most of the soluble matter was extracted and converted to the sulphates by heating with concentrated sulphuric acid, the excess of which was driven off. After this treatment the pulverised sulphates were dissolved in ice water. The solution was treated with potassium sulphate, the soluble double sulphates precipitated with oxalic acid, converted to the oxides, and then to the nitrates. The yttrium earths were then fractioned with sodium succinate, and in all respects appeared to be quite similar to those obtained from fergusonite. The atomic weights of the fractions were:—115·5, 112·7, 110·0, 108·2, 104·5, 102·5.

Gadolinite, from Texas.

300 grms. were treated with hydrofluoric acid, the insoluble fluorides converted to sulphates, the cerium didymium group removed by potassium sulphate as usual. Twenty-seven grms. of the oxides obtained were converted to the neutral nitrates and dissolved in 1 litre of water. This solution was fractionally precipitated with a 5 per cent solution of sodium succinate. The atomic weights of the various fractions were:—122·0, 117·0, 112·0, 112·0, 108·5, 103·0, 102·5. The absorption spectra showed that the earths varied in the same manner as did the atomic weights.

Keilhaute, from Tvedestrand, Norway.

1500 grms. of the mineral were treated with hydrofluoric acid. The insoluble fluorides were converted to the sulphates, and the sulphate solution submitted to treatment with potassium sulphate in order to remove the cerium-didymium group. Seventeen grms. of the oxides thus obtained were converted to the neutral nitrates, and diluted to 1 litre. This solution was fractioned with

a 5 per cent solution of sodium succinate. The fractions showed atomic weights of 116.5, 116.5, 108.0, 104.0, 104.0. In general, the atomic weights were somewhat higher than the earths from fergusonite, but in all other respects were found to be identical.

Department of the Succinates of the Erbium Earths.

The study of these minerals indicated that sodium succinate showed the same general behaviour towards different mixtures of the earths having low atomic weight. The separation seemed to be more marked as the average atomic weight of the mixture increased. In order to experimentally investigate this in more detail, erbium earths were extracted from monazite and samarskite. The erbium earths from monazite were separated from other members of the yttrium group by the chromate method. From a neutral nitrate solution containing 10 grms. of these oxides per litre, fractions were obtained by means of a 5 per cent sodium succinate solution. The atomic weights were:—152.5, 154, 148.5, 139, 124. A fraction of the samarskite earths, showing an atomic weight of 122.5 obtained by the succinate method, was converted to the neutral nitrates, and again fractioned by the sodium succinate method. The atomic weights of these fractions were as follows:—133.0, 134.0, 131, 127.0, 122.5, 112.5, 103.0, while the colour of the oxides varied from nearly white to brown. It was apparent, therefore, that the succinate method gave a more rapid separation with earths having comparatively high atomic weight.

Composition of Yttrium Succinate.

A few succinates have been made and analysed. Czudnowicz and Cleve (analysis given) report the succinate of lanthanum as $\text{La}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$ (*Bull. Soc. Chim.*, xxi., 202). Cleve reports the succinate of samarium (*Bull. Soc. Chim.*, xliii., 172), without analysis, as $\text{Sm}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, also the succinate of yttrium (*Bull. Soc. Chim.*, xviii., 296), with analysis, as $\text{Yt}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$, with analysis the succinate of erbium as $\text{Er}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ (*Bull. Soc. Chim.*, xliii., 172). Czudnowicz (*Fahresb.*, 1861, p. 189) tells how to make the succinate of cerium, and gives some of its properties. It is reported as $\text{Ce}(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 1.5\text{H}_2\text{O}$. Recently, Sir William Crookes made the succinate of scandium, to which he gave the formula $\text{Sc}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot \text{OH} \cdot \text{H}_2\text{O}$.

Yttrium was prepared in a fairly pure condition from mixed residues by the chromate method. The material selected gave only the slightest trace of absorption spectra when observed in a saturated solution 20 cm. thick. A neutral solution of this yttrium as nitrate was precipitated in a dilute solution at a boiling temperature by the addition of sodium succinate, drop by drop, with constant stirring. The precipitate was filtered, washed with boiling water, and dried over sulphuric acid until the weight was constant. The crystalline compound prepared in this manner was pure white. Analysis showed it to be a normal succinate.

Theoretical for $\text{Yt}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ Yt = 90.1.

		Theoretical.		Found.	
Yt		31.40		31.89	31.79
C		25.12		25.83	25.45
H		3.00		3.28	3.30

Solubility of Yttrium Succinate.

The salt was introduced into a flask with distilled water, connected with a reflex condenser, boiled for seven hours, and filtered hot. One litre, when evaporated to dryness in a platinum dish, gave 0.054 gm. of oxide, equivalent to 0.135 gm. of yttrium succinate. The same experiment was repeated, the boiling being continued in this instance for twenty-one hours, and showed a solubility of 0.152 gm. of the succinate. These determinations showed that the normal succinate was only sparingly soluble in

water. Qualitative observations seemed to indicate that the solubility was greatly affected by the presence of an excess of either yttrium nitrate or sodium succinate.

Conclusion.

As a precipitation method the use of the succinates can be highly recommended. The precipitates are readily handled, and by ignition converted to the oxides. Should it be desirable to conduct this separation on a scale in which the question of economy is to be considered, the succinates can easily be converted to the hydroxides by means of sodium hydroxide.

The best separation can be performed by precipitating a nearly neutral boiling solution of the nitrates with sodium succinate, added drop by drop. It makes very little difference whether the solution is stirred or not. As long as the concentration of the yttrium earths does not exceed 2 to 3 per cent the separation is satisfactory.

Yttrium succinate is a normal salt having the formula $\text{Yt}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. This is a white salt, slightly hygroscopic and very nearly insoluble in water, 0.0574 gm. of the oxide, equivalent to 0.1435 gm. of the succinate, being soluble in 1 litre of boiling water.

The author wishes at this time to express his thanks to Prof. Victor Lenher for valuable suggestions in this work, and to H. S. Miner, of the Welsbach Light Company, for a large part of the material.—*Journal of the American Chemical Society*, xxxiii., No. 1.

WATER SUPPLY.*

By JOHN H. BALFOUR BROWNE, K.C., D.L.

THE question of water supply is in one aspect a scientific one, and in another aspect a political one. The source of all water supply is evaporation, which raises and purifies water which is taken up from the land and the sea, which after condensation is returned to us as rain, dew, snow, and hoar frost, and these waters are to be found ready to our hand in springs, streams, lakes, and in the envelope of earth which is tapped by means of wells. In early days the water supply was a matter of hand to mouth. In the matter of water, at any rate, men drank water when they were thirsty—unlike the characters in Maeterlinck's "Palace of Happiness," who were, you will remember, the Luxury of Drinking when you are not Thirsty and of Eating when you are not Hungry. In the old days people, in relation to these ordinary articles of diet, acted upon the advice given in that old-world book "Sandford and Merton," and "only drank when they were dry." But even in the old days men in this country used water occasionally for washing, although the modern passion for baths had not developed in the dark ages, but even then there seems to have been a physiological cleanliness which the best advertised soap does not give. We find, however, that even in these early days there was a political aspect in water supply. The existence of springs in many cases determined the sites of cities. Many towns have been built on rivers partly because they were sources of water supply, but mostly when the rivers were navigable and afforded a highway for ships. Now, however, it is found that populations have increased to such an extent in certain localities, owing to the gregariousness of men and other political considerations, that the immediate sources have proved inadequate, and great towns in this country—like Rome in ancient days—have had to go a distance for their water supplies, and have had to construct great engineering works for the conveyance of water to the area of distribution. Water is at present collected and sold in England to a value of nearly £8,000,000 annually, and when it is delivered at the house of the consumer it costs him about 2d. a ton.

* A Discourse delivered before the Royal Institution, March 17, 1911

Aqueducts, or channels by which water is conveyed along an inclined plane, were known to the Greeks, but there are no remains of those they constructed. The Roman aqueducts were amongst the most important of their great works, and the present supply of Rome is still carried by these artificial rivers, sometimes through passages cut in the hills, sometimes on arches bridging the valleys and carrying the water across the plains. One of these aqueducts is 62 miles in length. We in this country have had to go even further afield for our water sources. A large portion (56 per cent) of the supply of Liverpool is brought from the river Vyrnwy, in North Wales, a distance 68 miles. Leicester is 60 miles from the sources of the Derwent Valley Water Board supply; Birmingham gets its water from Radnorshire, a distance of 71 miles; and Manchester from Thirlmere, by means of pipes and aqueducts, a distance of 96 miles. Paris derives some of its water from the Champagne district through pipes and aqueducts 80 miles in length, and some from Vanne, a distance of 104 miles. There has, too, been a suggestion that London should draw its public water supplies from Wales, which would involve carrying the water about 200 miles. This scheme was first suggested by Mr. Bateman in 1867. He proposed to collect the rainfall on 204 square miles, and, by means of an aqueduct 173 miles in length, to bring 230 million gallons of water a day to London, and he estimated the cost at £11,400,023. About the same time, too, there was a suggestion to carry the water of Ulleswater and Hawswater, which it was said could supply 550 million gallons a day from an area of 100 square miles, to the Metropolis, supplying Liverpool, Leeds, Bolton, Bury, Blackburn, Huddersfield, &c., on the way. These great ideas were of course too large to be realised in these small times, and many of these towns have, since the suggestion was made, supplied themselves with water by means of comparatively small scale works instead of becoming parties in a national undertaking.

The difficulty of meeting the demands of such large towns is obvious, from the fact that it involves such great works and such heavy expense to secure an adequate supply. To-day the ratepayers of Birmingham are paying not only water rates, but contributing out of the ordinary rates £64,000 a year to meet the heavy annual charges in connection with their Welsh scheme. Such a fact indicates that for places far from the sources of supply, and with wealth comparatively small to that of the great Midland towns, the difficulty of securing any supply for their future wants has become increasingly difficult, and may soon become impossible; and in this aspect the question of the future water supply of our populations becomes a significant political question, and because it is a matter of real importance to the health and trade of our great town populations, it has received no attention at all at the busy hands of our platform politicians. And yet, in my view, no matter is more worthy of serious consideration and attention, none which is more urgently practical, than the question of the future water supply of England. At one time England was able with its rich fields to feed its own populations, but, as trade prospered and populations increased, it was found impossible to produce food-stuffs sufficient for our people, and at present probably five-sixths of the total food of the people is imported from abroad. It is in this connection that current politics has taken in hand the problem how we are to continue to obtain these supplies from abroad; and while one school of politics thinks that the future is assured to us so long as the price of the loaf is not increased, another recognises the necessity of earning sufficient here, to enable us to buy our food in other markets. But in relation to water supply we are in a worse predicament. We must depend for that on the rainfall of our own lands, and the improvident way in which our sources have been squandered in the past, the way in which the long arm of wealth has been allowed to appropriate sources which may not naturally or geographically belong to the community in question, the exhaustion of local sources, and the waste of underground

water which takes place in connection with the mining operations of England, has much complicated the great question, and has made the future of Britain as to water supply both precarious and serious.

I have pointed out that the sources of supply are from springs, streams, and wells which tap the underground sources. There are in some quarters objections to rivers—full grown rivers—as a source of supply, largely due to the fact that communities with insanitary rashness and short-sightedness have thrown their refuse and filth into streams, and made them the carriers of sewage. This matter was fully discussed recently in Parliament when the Great Yarmouth Water Company endeavoured to secure an additional supply of water to the town beyond that which it then drew from Ormesby Broad. We know, of course, that the rainfall in the Eastern counties is much less than in the West of England and Wales, and the company had been advised by most competent engineers that the most suitable source of supply was from the River Bure. The population above the proposed intake was very small, only one person to four acres, but still it could not be said that no sewage did find its way into the river. But even this insanitary indiscretion is condoned by Nature, and rivers, especially rapid and turbulent streams, have a way of burning off effete matter which is put into its liquid charge. Whether this process of purification is absolutely effective or not is still a moot point, and chemists and bacteriologists are divided as to the safety in any case of drinking water which has been subject to sewage pollution. One gentleman holding that in a few miles a river will get rid of all sewage by its "cold ablation"; another that there is not a river in England long enough to get rid of a pathogenic germ. The great experiment of London has failed to convince some of these experts. London derives the bulk of its water from the Thames. In the Thames watershed, above the Water Board's intake, there are at least 1,000,000 people and about 800,000 other animals. The London water is supplied to nearly 7,000,000 people. This is obviously a large experiment, for there are about as many people in Water London as in the two kingdoms of Norway and Sweden, about the same population as there is in widespread Canada. The water mains of London, according to the chairman of the Board, would reach from London to New York and back; and yet, notwithstanding the supply of river water, the health of London is exceptionally good. Indeed there are some persons who seem to think that river water is really more wholesome than any other, and there is an interesting statistic produced in proof of this assertion. The death rate of Great Yarmouth, which, as I have said, now takes its water from the Bure, is 15 per 1000. Chester, which is supplied from the Dee, 15·4 per 1000; and Greater London, which drinks water from the Lea and the Thames, has a death rate of 13·3. But against this the death rate of the great towns which have pure hill waters for their supplies are, in the case of Birmingham, 15·9; Manchester, 18·2; and Liverpool, 19·2. If statistics were absolutely convincing, the case for river water as against hill water would seem to be made out. But we must weigh statistics, and not allow them merely to count. It might almost as reasonably be suggested by anyone, who was an opponent of municipal trading, that the results were due to the fact that in the three first cases the water was supplied by companies and in the three last by corporations.

But, apart from any such questions, it is obvious that Thames and Lea water as supplied to London is far from being an unsatisfactory drinking water. But it is only fair to remember that just as in economics there is no such thing as "raw material," so in the case of our raw waters the water as delivered is in most cases a manufactured article.

It was always understood that mere sedimentation carried down a certain number of the germs which were contained in water, but the experiments of Dr. Houston and others show that millions of these germs in water artificially infected with cholera vibrios are dead at the end

of a week's storage. (Dr. Houston has found, too, that even a week's storage of raw river water is an enormous protection against the "cultured" and "uncultured" bacilli of typhoid fever, and "that less than a month's storage is an absolute protection against typhoid fever").

It is under these circumstances that the Metropolitan Water Board has abandoned the idea of going to Wales for its supplementary water supply, and proposes, by a Bill in the present Parliament, to obtain power to construct a chain of reservoirs for the purpose of decanting the raw river water at Staines, and to spend £6,900,000 on this great scheme which is to supply the wants of Greater London for the next thirty years—until, indeed, the population of the Metropolis may be twelve millions.

But I was referring to the immense difficulty that any comparatively small town has in our days of securing a pure supply of hill water. So great is the difficulty that, as I have said, the Metropolitan Water Board has properly hesitated to go to Wales, having spent £47,000,000 in the acquisition of the London Water Companies—the enormous difficulties of a Welsh scheme seem to have been too great even for the gigantic financial resources of London. It is not, therefore, a matter for wonder that a town like Great Yarmouth has to look to some near source of supply for the further wants of the town, and as I have said they were advised to have recourse to the Bure. There were the usual objections to river water, and in this case it was urged that the river which drains the Broads is in summer the home of a large floating population in house-boats and other craft. It was, on the other hand, said that the same objection might be made against the Thames, for the Thames above the in-takes has, in a momentary lapse into poetic diction, been called "the water park of London." But here again the health of London was in evidence, and in the case of Yarmouth power was taken to prevent any house-boat anchoring within a considerable distance of the in-take.

There was another objection urged to the taking of water from the Bure for town supply. When the wind was in the north-west the waters of the German Ocean were heaped up by the spade-work of the gusts, and when that happened at the same time as a spring-tide the waters of the Bure were held or backed-up, and it was said that owing to the mixing action which takes place between sea and river water, the waters of the river at the point of in-take would be salt or brackish. It was argued that it was ridiculous to supply a river water impregnated with chloride of sodium to two towns like Yarmouth and Lowestoft. But here science came to the help of the water company. The occasions when the north-west winds and the high-spring tide synchronised were of course very rare, and it was proposed by the Bill that whenever such an event took place and when there were more than 20 grains of common salt to the gallon (that is in 70,000 parts) in the Bure water, the company should cease to pump from the river, and supply the town only from the stored water of the Ormesby Broad. Sir William Ramsay, too, invented for the occasion a little instrument. It was a small glass cell, containing two copper plates. This was to be sunk in the river, and as long as the plates were in contact with the fresh river water no electric current passed between the plates. But when salt water was substituted for fresh, and it was sufficiently salt to have 20 grains of chlorine to the gallon, an electric current passed and rang a bell. If this little apparatus was placed in the river two or three miles below the in-take, there would be timely warning of the uprush of the sea water, and it was explained that it could be made not only to ring a bell but to stop the pumping-engine. This apparatus was exhibited to the Lord's Committee, and, upon salt being added to the water, the bell rang. I remember one of the Counsel in the case who was a cynic said "Ah! Sir William, if you had been before the Royal Institution it would not have worked." That is the reason I have for not repeating the experiment before you to-night.

That 20 grains of chlorine to the gallon was not a serious

matter was proved by the statement that Apollinaris water, of which some of the members were partaking at their frugal lunch, contained 59 grains of chlorine to the gallon.

It may be of some use if I say something about the sources and methods of supply. There is nothing very new about water supply. Even in deep wells we have been anticipated; Joseph's Well at Cairo is 297 feet deep, and some of the Wells in China have gone to a depth of 1500 feet. In modern times we have in some cases been abandoning our well supplies. At one time almost the whole supply of Liverpool was drawn from wells in the New Red Sandstone. To-day she only draws 7·36 per cent from wells—36·42 per cent from Rivington, and 56·22 per cent from Vyrnwy. There is a well at Passy, near Paris, 1923 feet deep, and it delivers $5\frac{1}{2}$ million gallons of water a day. In South Dakota there is a well which penetrates the earth's crust 725 feet and raises 111 million gallons a day. In relation to the purity of such underground supplies, many of them in this country are derived from the chalk, and it is interesting to note the precautions which Nature has taken to purify such supplies. It is found that such soils as chalk breathe air and expel gases just as the human lungs do. The breathing is long-drawn and irregular and depends mainly on the barometric pressure of the atmosphere. But that such breathing takes place can be shown by the simple experiment of closing the folding doors over a chalk well and holding a lighted candle to the bucket rope hole, and the sensitive flare will show the indraft or outdraft as the case may be; which varies, of course, in intensity according to the extent of recent barometric changes. When water has to be got from under-ground sources, then a well has to be sunk, adits driven, a pump established, and the water raised to the clear water-tank. In some cases, however, Nature not only does the purification of our water by its chalk lungs, but does our pumping for us. The artesian well which gets its name from Artois in France, is a well which is sunk to a pervious water-bearing strata lying between two impervious layers. In that case the water falling on the surface and getting into the ground will, when the well is sunk through the surface impervious stratum, rise to the surface, Nature doing the lifting for us.

But not only have we been anticipated in the matter of wells, in aqueducts we are mere imitators of our predecessors, who even understood, it is obvious, the principle of the inverted syphon, as it is called, by means of which water is carried in pipes across valleys running down hill on the one side and up hill on the other; for Lyons, in France, was supplied long ago by means of lead pipes from 12 to 18 inches in diameter, 9 miles in length, and worked under a head of 200 feet. It is true that the favourite method of engineers before the nineteenth century, when cast-iron pipes came into use, was to cross valleys by bridge aqueducts, and this, apparently on the ground that the materials of their pipes (either trunks of elm trees hollowed out, from which our word "trunk main" has survived to us, or lead) did not lend themselves to the conveyance of large volumes of water as the ordinary aqueduct did. The favourite system of supply in this country to-day is undoubtedly by means of a gravitation system, either from natural lakes like Loch Katrine or Thirlmere, or from artificial lakes—or, as they are called, "impounding reservoirs." These reservoirs, by means of a dam formerly formed of earth, with a core of impervious puddled clay, but now more frequently of masonry, catch and impound the water which falls upon the gathering ground. Of course it is desirable to avoid a gathering ground which consists of cultivated land or upon which there is any considerable population. The best gathering ground is one which is composed of impervious rocks—for porous strata steal too much water and which is covered only with mountain pasture or moorland. In many cases no objection is made to the existence of sheep upon the gathering ground; but Liverpool, in the case of its Rivington works, has purchased the whole of the gathering ground, and, after destroying and pulling down many of

the farms and buildings, has kept a great part of the gathering ground free from sheep and let it to a sporting tenant. The largest gathering ground in this country dealt with by water works is the Birmingham gathering ground, which will collect the water from 44,000 acres, while the Thirlmere scheme of the Manchester Corporation has only a contributory area of 11,000 acres, and the Vyrnwy works of Liverpool Corporation only 22,000 acres.

Hundreds of dams have been built in this country to collect the waters from gathering grounds in connection with water supply to towns, or water supply to canals and waterways. The wall which impounds the water at Vyrnwy is 85 feet high. The Manchester Corporation, which had to deal with a natural reservoir, constructed a dam only 50 feet in height, but the masonry embankment at Caban Coch, the reservoir of the Birmingham Corporation, is 122 feet high above the bed of the river; and some of the other dams of that great scheme, when complete, will be 128, 120, 101, and 98. These walls, of course, have behind them immense quantities of water varying from 8000 million gallons, in the case of Birmingham, down to very small number of gallons which run down a mill goit. The tensile strain or tear of such a mass of water as that at Caban Coch is enormous, and in that case the work is strong enough to bear such a strain up to 12 tons per square foot. The Bouzay dam, near Epinal in France, which was bad in design and faulty in construction, gave way with the pressure of $1\frac{1}{2}$ tons to the square foot.

On January 13 of this year a dam of a reservoir containing 250,000 cubic metres of water, which belonged to the Huelva Copper and Sulphur Company, Spain, owing, it is said, to a hidden spring under the masonry, gave way, and eleven people were drowned. That is near to-day, and affects us like a new wound. But even if none of us have memories which go back to 1849, tradition has told us of the bursting of the Bradfield Reservoir, which drowned the town of Sheffield, and put the country round for a distance of 12 or 14 miles under water. In that catastrophe 250 lives were lost, and property was destroyed to the extent of £327,000 in value. The Holmfirth Reservoir, which had an embankment 90 feet high and 150 yards long, after heavy rains burst in 1854, and 100 people were drowned in that night, and property valued at £600,000 was destroyed. In most of these cases, however, the calamity can be traced to the defective engineering skill which went to the construction, or subsequent carelessness in the maintenance. But many engineers would tell you that they have sleepless nights when one of these great cauldrons are filling with water for the first time—and people in the valleys below may well hold their breath until the stability of these great walls has been proved. In the case of the Bradfield Reservoir the burst reservoir filled the Don Valley with a mad flood. In the town of Sheffield the water rose to the height of the roofs of low buildings. Dead cattle were carried down by the waters, and in some cases deposited on house-tops, and, as in the days of Horace, "fishes roosted in elms." One incident of that great calamity is not uninteresting. When the flood was at its highest an old box-cradle came sailing on the dirty waters, and in it there was an infant safe asleep. No one claimed the little Noah, or his ark; no one knew what had become of its father or mother, although it was assumed that they and all who knew the new comer, were amongst that 250 dead. The parish had to adopt the foundling, and with a sense of propriety which is rare in parish authorities, they had the boy christened John Flood.

(A diagram was exhibited showing the position of the dam and the impounded water in the reservoir).

The water there stored in the supposed case has to supply the town, but has also to supply what is called the compensation water to the stream. Before the reservoir was formed, the riparian owners had all the water that fell on the gathering ground passing their land. Now, how-

ever, that the reservoir is there, the greater part of the water is to be carried away in pipes and supplied to the towns. The Waterworks Clauses Act, 1847, seemed to contemplate the compensation of any person who was injured by the construction of the works, by which the water was diverted, in money; but it has been found more convenient to compensate them in water. The arrangement usually made in such cases is that by a careful compilation from the rain gauges on or near the gathering ground, or from gaugings of the stream at the site of the embankment, the amount of water which flowed down the stream and is available for supply is ascertained. If this amount is calculated from the careful statistics of Dr. Mill, or from rain gauges, calculations have to be made as to the amount that is lost to the stream by evaporation or absorption, and even then the calculations have to be carried further to ascertain the amount which could be obtained by storage in three consecutive dry years. When the amount of storage water has been arrived at in inches of rainfall per annum, it is usual to give one-third of the rainfall in compensation to the stream, and take two-thirds for the town supply. At first sight this seems an unfair bargain, like the lawyer who takes the oyster and gives the client the shell. Here is the town taking the whole of the water and paying the owner by giving him back one-third. But the effect of such a bargain is clearly beneficial to the riparian owners. The promoters have to make a greater reservoir than would be necessary for the town supply in order to store the winter floods, and have to find the capital for that. By storing the winter floods in the reservoir, the riparian owners, who have land liable to flooding, are benefited, and those who use it for power are doubly benefited, for their mills are not drowned for so long a period in winter, and by reason of the compensation water, which, of course, much exceeds the minimum flow of the stream before the construction of the reservoir, they get more worth out of the water in the summer. It means, therefore, that the bargain which had been given effect to in a hundred Acts of Parliament is a fair one after all. But even when the amount of compensation has been determined, there have to be elaborate provisions and arrangements to secure the due discharge of the right number of gallons. The scheme has, even after the compensation has been discharged, to provide for the conveyance of the water to the area of distribution. That is done by means of a conduit.

(To be continued).

NOTICES OF BOOKS.

Metropolitan Borough of Poplar. Annual Report for the Year 1910. By FREDK. WM. ALEXANDER.

THIS report contains details of the output, cost, &c., of the electrolytic fluid which is distributed to the public to be used as a disinfectant. The returns are highly satisfactory, whether regarded from the point of view of economy or efficiency, and the results of the tests which are to be made at various schools in the Borough will be awaited with interest. The plant has recently been thoroughly overhauled, and has been found to be in excellent condition.

The Chemistry of the Coal Tar Dyes. By IRVING W. FAY, Ph.D. (Berlin). London: Constable and Co., Ltd. 1911. (16s. net).

THE constitution of the coal-tar dyes is discussed in some detail in this book, special emphasis being laid on the historical aspects of the development of our knowledge of the subject. The somewhat complicated structures of the principal dyes and their derivatives are made clear by tabular statements and formulæ, and proofs of the

composition of some dyes are given in full. Some manufacturing processes are included for description, and the short course of experimental work should give the student some insight into methods of preparation and the reactions of the dyes. This practical work includes only those manipulations and processes which would probably be familiar to the average student who had done a little organic chemistry. A chapter is devoted to the seven food colours which are permitted by the United States Government.

A Report of the Work of the Laboratories in 1910. By A. LUCAS, F.I.C. Cairo: National Printing Department. 1911. (5 P.T.).

THIS report gives a brief account of the chemical and physical testing of materials such as cements and building stones, the photometrical examination of illuminating gas, and the microscopical and chemical analysis of various articles of food which have been carried out in the Egyptian Survey Department Laboratories in 1910. The staff of the laboratories also find time to do a certain amount of research work, and lists are given of the papers they have published, mainly on subjects of special local interest, since 1902.

Ricerche Sull' Elio. ("Researches on Helium"). By Prof. ARNALDO PIUTTI. Rome: G. Bertero. 1911.

THE work which has been done by the chemists and physicists of all nations upon helium, regarding it more particularly as a degradation product of the radio-active elements, is lucidly discussed in this pamphlet, which is an extract from the *Transactions* of the Italian Society for the Advancement of Science. Many analyses are given of minerals containing helium, with reproduction of their spectra, and the author summarises clearly the results which have been already obtained.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other is expressed.

Bulletin de la Société Chimique de France.
Vol. ix.-x., No. 15, 1911.

Action of Aromatic Acetones on the Monosodium Derivative of Benzyl Cyanide.—F. Bodroux.—Benzophenone reacts violently with the sodium derivative of benzyl cyanide, the product being 1.1.2-triphenyl-acrylic nitrile, which the author identified by converting it into triphenyl-acrylic amide. Paramethylbenzophenone reacts equally energetically, but the action is far less violent in the case of α -naphthylphenyl-ketone, and dibenzylidene acetone hardly reacts at all.

***p*-Oxyphenylglyoxylic Acid.**—J. Aloy and Ch. Rabaut.—The oxidation of *p*-acetyl-amino-acetylbenzene gives *p*-acetylaminophenylglyoxylic acid, which may be converted into *p*-aminophenylglyoxylic acid by prolonged boiling with dilute HCl, followed by evaporation to dryness on the water-bath. When diazotised the amino-acid is transformed into *p*-oxyphenylglyoxylic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COOH}$. *p*-Oxyphenylacetic acid is obtained from this last acid by treatment with concentrated hydriodic acid.

Hydrogenation in Presence of Divided Palladium.—P. Breteau.—Phenanthrene can be converted into its tetrahydride by hydrogenation in presence of palladium-

black, prepared by reducing a palladous salt with formol. Phenanthrene can also be hydrogenated by dissolving zinc in hydrochloric acid in presence of precipitated palladium; the tetrahydride is the sole product, and it is also formed by electrolytic hydrogenation with a cathode of spongy palladium.

Pyridino-pentachloroiridates.—M. Delépine.—The oxidation of the pyridino-pentachloroiridites by chlorine, nitric acid, or aqua regia gives the pyridinopentachloroiridates. The alkaline salts are more or less dark red and crystalline; their solubilities follow the same order as those of the chloro-iridates. They yield organic salts with primary fatty amines, benzylamine, &c. If an acidulated solution of a pyridino-pentachloroiridate is shaken with amyl alcohol a magnificent violet colouration is obtained; this constitutes an excellent test for them. They are very stable towards acids, but readily give iridescent salts with alkalis.

Constitution of Oxy-indazols.—P. Freundler.—The author has established the following facts concerning the constitution of the chlorinated oxyindazols:—(1) An indazylic nucleus exists in them; (2) an OH group is present in the 7-position; (3) the halogen atoms occur in the 3- and 5-positions of the first nucleus.

Zeitschrift für Anorganische Chemie.
Vol. lxxi., No. 3, 1911.

Potassium Barium Orthosulpharsenate.—E. Glatzel.—Potassium barium orthosulpharsenate, $\text{KBaAsS}_4 \cdot 6\text{H}_2\text{O}$, can be prepared by adding barium orthosulpharsenate to an aqueous solution of potassium chloride, and concentrating the solution. The double salt then separates out in crystals, which are quite transparent when freshly prepared, but become white or light yellow when they are allowed to stand. They are readily soluble in water, and are decomposed by acids, giving arsenic pentasulphide.

Compounds of Silver with Cadmium.—G. J. Petrenko and A. S. Fedorow. By thermic and microscopical experiments, the authors found that a compound, AgCd_3 , exists, but quenching experiments have not confirmed this result.

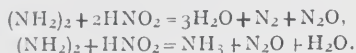
Titration of Potassium Cyanide in presence of Potassium Ferrocyanide.—W. D. Treadwell.—Potassium cyanide can be determined in presence of potassium ferrocyanide in dilute faintly alkaline solution by means of silver nitrate, about 0.1 grm. of potassium iodide being used as indicator. Soluble ferricyanides have an oxidising action in alkaline solution on potassium cyanide, but the cyanate formed does not affect the titration of the cyanide.

Holmium.—Otto Holmberg.—The author used 29 kgrms. of euxenite as his initial material for the preparation of holmium. He opened it up with sulphuric acid, dissolved the residue in cold water, and precipitated with ammonia. The precipitate was dissolved in nitric acid and boiled, the mineral acids were filtered off, and the solution precipitated with oxalic acid. The oxalates were treated with boiling ammonium oxalate, when most of the holmium remained undissolved. The residue was then fractionated with *m*-nitrobenzosulphonic acid, and thus the holmium was concentrated in the difficultly soluble fractions, which were converted into nitrate, treated with bismuth nitrate, and again fractionated. By this method holmium material was obtained, and was further purified by a repetition of the ammonium oxalate process. Atomic weight determinations gave $\text{Ho} = 163.5$. Thus holmium takes its place between dysprosium and erbium in the series of the rare earths.

Volumetric Determination of Iron and Vanadium Present Together.—Erich Müller and Otto Diefenthaler.—To determine iron and vanadium in ferrovandium

about 1 grm. of the alloy is dissolved in a covered beaker in nitric acid, the excess of nitric acid is evaporated off with a little hydrochloric acid, and the solution is gently boiled with 20 cc. of HCl and 50 cc. of alcohol. The solution is evaporated to about 5 cc. on the water-bath, and then made up to a known volume. The iron is determined iodometrically in an aliquot part, and the rest titrated with 1/10 N-permanganate to determine the vanadium.

Action of Hydrazine Sulphate on Nitrites and a New Method of Determining Nitrogen in Nitrites.—Biman Behary Dey and Hemendra Kumar Sen.—Hydrazine acts on nitrites according to the two following equations:—



Thus three molecules of HNO_2 gave one molecule of nitrogen and two of N_2O . This action provides a simple method of determining the nitrogen in nitrites.

Compounds of Ammonia and Water.—A. Smits and S. Postma.—The authors have determined the melting-points of mixtures of ammonia and water, and have detected two maxima at -77° and -78° , corresponding to the compounds $\text{NH}_3 + \text{H}_2\text{O}$ or NH_4OH , and $2\text{NH}_3 + \text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{O}$ respectively. This proves the existence of these two compounds.

Periodides and Perbromides of Metals of Alkaline Earths.—W. Herz and Alfred Bulla.—Varying amounts of iodine or bromine were added to aqueous solutions of barium calcium or strontium iodide, and the solutions were shaken with carbon tetrachloride at 25°C . The free iodine or bromine could be calculated from the amount taken up by the tetrachloride, and hence the periodide or perbromide formed according to the equation $\text{BaI}_2 + \text{I}_2 \rightleftharpoons \text{BaI}_4$ could be determined.

Formation of Compounds of Chlorides of Cu, Pb, Fe, Zn, Sn, and Bi.—Gottfried Herrmann.—Tamman has formulated the following two rules in connection with the formation of compounds of metals with metals:—1. Elements of a natural group rarely form compounds with one another. 2. Any purely metallic element either forms compounds with all the metals of a given natural group, or with none of them. The author has investigated the melting-point curves of the binary combinations of the seven chlorides, PbCl_2 , BiCl_3 , CdCl_2 , Cu_2Cl_2 , ZnCl_2 , SnCl_2 , and FeCl_3 , and gives his results in tabular form. The first of the rules holds good for these salts, but not the second. There appears to be no parallelism between the power of the metals to form compounds with one another and the corresponding power of their salts to combine.

Action of Alkyl Iodides on Copper Oxide.—H. G. Denham.—Copper oxide reacts with methyl iodide at 310° , but the reaction does not taken place according to the equation $\text{CuO} + 2\text{CH}_3\text{I} \rightarrow \text{CuI}_2 + (\text{CH}_3)_2\text{O}$, for the solid product obtained always consists of cuprous iodide, which appears to be the primary product of the reaction. Many other substances are formed. Thus the distillate gives the reactions of aldehyde and CO , C_2H_4 , and CH_4 , and its homologues are evolved.

Separation of Cerium by Potassium Permanganate.—Edwin J. Roberts.—The solution of the nitrates of the rare earths is heated in a large dish, and if necessary neutralised with sodium carbonate solution; then a solution of potassium permanganate is added till the red colouration is permanent, when a solution containing permanganate (one molecule) and sodium carbonate (four molecules) is added. The liquid is boiled, and when the colour has quite disappeared pure permanganate is added. The acidity of the solution must be tested from time to time, and it must be made neutral to litmus by the addition of the mixed solution of sodium carbonate. The solution is then heated and filtered while hot, and if the filtrate is neutral all the cerium is precipitated.

Action of Ammonia on Mercurous Nitrate.—Haridas Saha and Kumud Nath Choudhuri.—The black substance which is formed when mercurous nitrate and ammonia react consists of a mixture of metallic mercury and a white substance of empirical formula $\text{N}_2\text{Hg}_2\text{H}_4\text{O}_5$. This last substance is readily soluble in strong ammonia.

Atti della Reale Accademia dei Lincei.
Vol. xx., (II.), No. 2, 1911.

Synthesis of Pyrazolones of a Compound of γ -Pyrone.—F. Carlo Palazzo and Raffaele Liverani.—The action of various hydrazines (diamide, phenylhydrazine, semicarbazide) on a compound of γ -pyrone, Guthzeit's ether, $\text{C}_{13}\text{H}_{16}\text{O}_6$ ($\alpha\alpha'$ -dimethyl- γ -pyrone- $\beta\beta'$ -dicarbonic ether), gives a mixture of products which cannot always be separated easily. In the case of hydrazine hydrate three products were obtained, all belonging to the pyrazolone group:—(1) A product, $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_3$, fusing at 195 – 196° ; (2) a product, possibly isomeric with the above, fusing at 125 – 130° ; (3) a product, $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_4$, fusing at 142 – 145° .

Thermic Analysis of Binary Mixtures of Chlorides of Divalent Metals.—C. Sandonnini and G. Scarpa.—Stannous chloride and lead chloride give mixed crystals in all proportions, as do also cadmium chloride and manganous chloride. Cadmium chloride and stannous chloride give a single eutectic and mixtures of manganous chloride with stannous chloride and lead chloride behave similarly.

MEETINGS FOR THE WEEK.

WEDNESDAY, NOV. 1ST.—Society of Public Analysts, 8. "Shrewsbury and Knapp's Process for Estimating Coconut Oil," by H. S. Shrewsbury and A. W. Knapp. "A Counterfeit Gold Coin," by H. S. Shrewsbury. "Examination of Finnish Turpentine," by L. M. Nash. "Approximate Estimation of Starch by Iodine," by L. Reed. "Gravimetric Estimation of Phosphorus in Milk," by E. H. Miller. "Robert's Reagent as a Test for Salicylic Acid," by J. McCrae. "Precipitation of Nickel Compounds and Preparation of Spongy Nickel," by W. H. Low.

THURSDAY, 2ND.—Royal Society. "Colour Blindness and the Trichromatic Theory of Colour Vision—Part III., Incomplete Colour Blindness," by Sir W. de W. Abney. "Iridescent Colours of Birds and Insects," by A. Mallock. "Behaviour of the Infusorian Micronucleus in Regeneration," by K. K. Lewin. "An Inquiry into the Influence of the Constituents of a Bacterial Emulsion on the Opsonic Index," by A. F. Hayden and W. P. Morgan. "Morphology of *Trypanosoma gambiense* (Dutton and Todd)," by Col. Sir David Bruce. "Factors in the Interpretation of the Inhibitive and Fixation Serum Reactions in Pulmonary Tuberculosis" and "Preliminary Report upon the Injection of Rabbits with Protein-free (tuberculo-) Antigen and Antigen-serum Mixtures," by A. H. Caulfield.

Chemical, 8.30. "Constituents of the Seeds of *Cuscuta edulis*," by F. B. Power and L. Callen. "Preparation of the Betaine of Tryptophane and its identity with the Alkaloid Hypaphorine," by P. von Romburgh and G. Barger. " β -2-Methoxynaphthylpropionic Acid and Methoxy-*peri*-naphth-1-anonic," by G. Barger and W. W. Starling. "Dihydroxydihydrindylamine and its Resolution into Optically Active Components," by W. J. Pope and J. Read. "Studies in Phototropy and Thermotropy—Part II., Naphthylidenamines," by A. Senier and R. Clarke. "Some Derivatives of 4-(or 5)-Methylglutamine," by A. J. Ewins. "Stability of the Double Oxalates of Sodium and Nickel, and Sodium and Cobalt," by J. W. Dodgson. "The Lower Limit of Inflammation of Mixtures of the Paraffin Hydrocarbons with Air," by M. J. Burgess and R. V. Wheeler.

THE CHEMICAL NEWS.

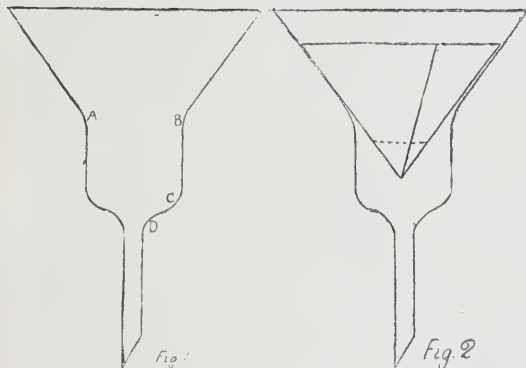
VOL. CIV., No. 2710.

A NEW FUNNEL. (SECOND COMMUNICATION).

By PHILIP BLACKMAN.

AN important improvement upon the funnel described in the CHEMICAL NEWS, 1911, CIV., 30, has been effected, viz., the bends at B, C, and D are rounded off, thus adding greatly to the strength of the funnel. (In ordinary funnels these bends are sharp, and in consequence are a great source of weakness, the stems easily breaking off from the bodies on shock or sudden changes of temperature, e.g., the pouring of a hot liquid on to the colder funnel).

Experiments have been carried out with these funnels, and their time efficiencies compared with that of a plain (ordinary) funnel under varying conditions. It will be seen that in all cases under similar conditions filtration takes place much more rapidly with these funnels than with the other, and this rapidly obviously must render the process of filtering a much easier and more perfect and complete operation. The reason for this greatly accelerated filtering is that a great part of the filter cone, all or nearly all that part containing liquid or precipitate, is suspended, and has no contact with the funnel, thus allowing



unimpeded passage of liquid through the filter pores. (In an ordinary funnel the filter-paper fits closely the funnel sides, and in consequence the passage of liquid through the paper is greatly retarded, making the process of filtering a slow and tedious task).

This funnel is much more easily kept clean, and also acts quicker, than a ribbed (or fluted) funnel.

It is as well to point out that a small filter-paper should not be used with a large-sized funnel. If this precaution be observed there is not the slightest danger of the filter slipping downwards; in the author's numerous experiments such mishap did not occur once.

This funnel, in various sizes, is manufactured and supplied by Messrs. Townson and Mercer, 34, Camomile Street, London, E.C.

Results.

I. In each test water was passed through the filter and the time was measured to collect 750 cc. In each case the water was maintained continually to $\frac{1}{2}$ inch of the filter edge. There were no precipitates in the filter-paper.

Kind of funnel.	Size A to B (inches).	Time (minutes).	Efficiency.
Plain	—	48	1.0
Blackman ..	I	26	1.8
Blackman ..	$1\frac{1}{2}$	21	2.2
Blackman ..	$1\frac{3}{4}$	17	2.8

II. 2.95 grms. of finely-powdered calcium carbonate was placed in each filter-paper, and the quantities of water passed through and collected in ninety minutes were measured. In the case of the "1-inch" funnel shown five-sixths (in height) of the unsupported filter-cone was filled with the material. Generally, in quantitative work, nothing like so great a weight as 2.95 grms. would be placed within a filter-paper, and, had smaller quantities of the material been used in the experiments, obviously (because the extents of the filter-cones not covered with the substance would have been respectively greater) the efficiencies as given above would have been still greater for (i.e., much more in favour of) these funnels. The water was maintained continually to within $\frac{1}{2}$ inch of the edges of the filter-papers.

Kind of funnel.	Size A to B (inches).	Water (cc.).	Efficiency.
Plain	—	390	1.0
Blackman ..	I	495	1.2
Blackman ..	$1\frac{1}{2}$	605	1.5
Blackman ..	$1\frac{3}{4}$	780	2.0

III. Using the filter-papers and contained calcium carbonate in Experiment II., the times taken to collect 750 cc. of water were measured, the water being always kept to within $\frac{1}{2}$ of an inch from the filter edges.

Kind of funnel.	Size A to B (inches).	Time (minutes).	Efficiency.
Plain	—	175	1.0
Blackman ..	I	138	1.3
Blackman ..	$1\frac{1}{2}$	103	1.6
Blackman ..	$1\frac{3}{4}$	80	2.2

33a, Princess May Road,
London, N.

A FUNNEL SUPPORT.

(SECOND COMMUNICATION).

By PHILIP BLACKMAN.

THE support described in the CHEMICAL NEWS, 1911, CIV., 31, is made of aluminium and not of glass. After careful consideration it has been decided to abandon glass as the material for the following reasons. On account of the circular flutes or ribs it would have to be made by a process which would render it very brittle and easily breakable on the slightest shock or sudden change of temperature, and the breakage in storage would be great.

The support consists of a circular disc, in various sizes (from 4 to 12 inches in diameter), with a number of concentric circular flutes or ribs, and having at the centre an upright tube (one inch in length and not less than three-quarters of an inch in the narrowest part), each end of which is funnel-shaped, so that a funnel may rest in it without shaking. It will fit any beaker or other wide-mouthed vessel of smaller diameter than itself, will hold any sized funnel, and may be used in upright or inverted position.

These aluminium funnel-supports are manufactured and supplied by Messrs. Townson and Mercer, 34, Camomile Street, London, E.C.

Society of Chemical Industry.—At the meeting of the London Section of the Society to be held at 8 p.m. on Monday, November 6th, at Burlington House, Dr. E. G. Acheson, of New York, will read a paper on "Deflocculation as affecting Lubrication." Dr. Acheson is well known as the inventor of lubricants consisting of deflocculated graphite—"Aquadag" and "Oildag" of carborundum, &c. The paper should be of interest to all who are concerned with lubrication and lubricants.

A DETERMINATION OF THE RATIO BETWEEN CHLORINE AND BROMINE AND SODIUM.*

By JACOB S. GOLDBAUM.

Introduction.

BEFORE the National Academy of Sciences, Wolcott Gibbs, in 1880, first suggested the use of mercury as cathode in electro analysis. His experiments, although purely qualitative, were sufficient to indicate the correctness of the principle involved. The subsequent development of the mercury cathode cell in metal determinations furnishes an important chapter in the history of analytical chemistry, but it is to its extension into the domain of anion estimation that especial attention is now directed.

Vortmann (*Elektrochem. Zeit.*, i., 137) and later Specketer (*Zeit. für Elektrochem.*, iv., 539) had published brief accounts of halogen fixation, but the activities of Edgar F. Smith and his students in the use of an attackable silver anode with a mercury cathode, made for sure and steady advance in this phase of our science. Within the last decade much has been published of results obtained in the John Harrison Laboratory of Chemistry in the analysis of alkali and alkaline earth salts with particular emphasis upon the halides of these metals. The advent of the "double cup" as devised by Hildebrand was important and timely. By its use many analyses and separations of decided interest have been effected, as is evident by reference to the work of Hildebrand (*Journ. Am. Chem. Soc.*, xxix., 447), McCutcheon (*Journ. Am. Chem. Soc.*, xxix., 1445), McCutcheon and Smith (*Journ. Am. Chem. Soc.*, xxix., 1460), Lukens and Smith (*Journ. Am. Chem. Soc.*, xxix., 1455), Kollock and Smith (*Proc. Am. Phil. Soc.*, xlv., 347), and Goldbaum and Smith (*Journ. Am. Chem. Soc.*, xxx., 1705; xxxi., 900; and xxxii., 1468).

Extreme accuracy has always been a feature of the values obtained in the papers mentioned above. It seems, however, that in the hands of other investigators, difficulty in duplicating results is being encountered from time to time. In the manipulation of the method there are many points of detail that heretofore have not been fully discussed. These have been more thoroughly studied in the present work. It is hoped that with the publication of this paper the mode of procedure will be made clear, and the reliability of the method established beyond further doubt. This paper aims to indicate the application of electrolysis in general, and of the method in particular, to the highly exacting field of atomic weight work, itself the severest test to which any analytical procedure can be subjected. Full appreciation is held of the remarkably trustworthy character of the present values of the atomic weights of the halogen elements. It was therefore not in a spirit of revision, but rather with the idea of attacking the problem from an entirely different and novel standpoint that this work was undertaken.

Fundamentally the principle employed is extremely simple. An aqueous solution of common salt, for example, is electrolysed with a weighed silver anode and mercury cathode. Sodium as cation forms an amalgam, chlorine attaches itself firmly to the silver, and the increase in weight of the anode represents the halogen content of the salt. In his monumental work on atomic weights, Berzelius always laid especial stress on "simplicity of analysis or synthesis of the simplest compounds." This dictum furnishes the keynote of the present investigation.

The many publications of atomic weight values of chlorine and bromine made within quite recent years contain admirable *résumés* of all methods heretofore employed, together with a listing of the results obtained by various investigators. It is hence deemed unnecessary to adopt a like procedure in this paper, and reference to "A Recalculation of the Atomic Weights," by F. W. Clarke (Smithsonian Institution Publication, 1900), is recommended.

Experimental Part.

Apparatus.—The electrolytic cell resembles in principle that used in the Castner-Kellner process for the decomposition of salt. It consists of a glass crystallising dish 16 cm. in diameter, 6 cm. high, in which is placed a bottomless beaker 5 cm. high and 7 cm. in diameter. An equilateral triangle of thin glass rod with one angle left open acts as a spring to hold the beaker firmly in the centre of the outer dish, and likewise permits of easy adjustment of the lower rim of the beaker to within about 4 mm. from the bottom of the crystallising dish. A layer of mercury 1 cm. in thickness (depth) placed in this immediately forms a two-compartment cell with the mercury as a seal. Extending around the inside of the outer compartment, about 1 cm. above the level of the mercury, is a ring of platinum wire holding a prong of the same metal which dips in the mercury. A stout platinum wire, partially encased in glass and held in position by a support clamped to glass stand, serves as cathode connection for the mercury with the negative pole of the circuit. The cell is covered with two semi-circular well fitting glass plates. The centre of each plate is notched and ground to admit the anode when the cover glasses are in position. Actual contact of the ground glass with the platinum anode is prevented by a protective platinum foil.

Special attention must be paid to the form of anode used. As finally adopted this consists of three circular discs of platinum gauze 5 cm. in diameter and 30 meshes per cm., the circumference of each being slightly fused. They are mounted 8 mm. apart on a platinum rod 1 mm. in diameter and 10 cm. long, which passes through the centres of the discs perpendicular to them. The silver plating of the anode will be discussed later. Rotation of the anode is accomplished by fastening it into the shaft of the special kind of motor used for all rotating work in this laboratory (see Smith's "Electro-analysis," 4th Ed., p. 58; the motor used was of the type listed by Greiner and Friederichs as No. 2159). The chuck of the shaft with which the anode came in contact is lined with new platinum foil. The shaft of the motor is connected by ordinary annunciator wire to the positive pole of the battery.

A Weston milliammeter, a Weston voltmeter (graduated to 0.5 v.), and a very efficient Ward-Leonard rheostat are placed in the circuit. The current is derived from a battery of ordinary storage cells.

An electric oven for drying the anode was constructed as follows:—Two ordinary iron tripods were fastened bottom to bottom to form a hollow cylinder 22 cm. long and 8 cm. in diameter. "Nichrome" ribbon, 1/16 inch wide, 0.0035 inch thick, with a resistance of 2 ohms per foot, was then wound round the asbestos-insulated tripod rods, and the cylinder, with suitable precautions, covered with previously ignited sheets of asbestos. The whole was subsequently placed in a wooden box 28 cm. high and 20 cm. square. On the bottom of the box were four stout corks on which rested a square of asbestos board. The oven was placed on this, and the sides of the box tightly packed with a mixture of plaster of paris and calcined magnesia. The bottom of the oven proper was covered with a sheet of ignited muscovite, and the interior space of the oven protected from the "nichrome" wire by sheets of the same material. Mica likewise formed the cover of the heating device. The oven had a resistance of 60.0 ohms, so that when connected with the ordinary lighting circuit of 110 volts d. c., it gave a temperature suitable for the purpose. This temperature was, of course, cumulative, and in the course of two hours rose steadily to 400°. The insulation served so well that the encasing wooden box was at all times comfortable to the touch. By means of an ordinary screw clamp held on a retort stand, the anode may be lowered into the clean interior of the oven. New platinum foil protected the rod of the anode from the iron screw clamp.

A nephelometer as devised and described by Richards

* From the *Journal of the American Chemical Society*, xxxiii., No. 1.

and Wells (*Am. Chem. Journ.*, xxxi., 235) served to determine the amount of dissolved silver halide.

The balance used was of an excellent Troemner design. It was kept in a room isolated from the rest of the laboratory. Successive weighings on it of the same object gave concordance to within 0.03 mgrm. The weights used were of exceptionally good make, the corrections as applied from the calibration according to the method of Richards being quite small (*Journ. Am. Chem. Soc.*, xxii., 144).

Preparation of Pure Materials.

Water.—The distilled water of the laboratory, on examination, contained no chlorides. Traces of organic matter present were destroyed by re-distillation from a weakly alkaline permanganate solution, using a block-tin condenser. The first part of the distillate was rejected, and the subsequent portions collected in Jena flasks. This water was then again distilled just as needed, and was never in contact with the glass for more than twenty-four hours before use.

Sodium Chloride.—Richards and Wells have conclusively shown that the preparation of pure sodium chloride is comparatively easy (*Journ. Am. Chem. Soc.*, xxvii., 459). The sodium chloride used in this work was obtained from the J. T. Baker Company, and was of exceptionally high grade. It was dissolved in pure water, and saturated with HCl gas (made from the purest commercial hydrochloric acid and pure concentrated sulphuric acid). The crystals of sodium chloride were then filtered and separated from the mother-liquor by centrifugal drainage, using a very efficient home-made centrifuge. They were again dissolved, and the entire operation twice repeated. After centrifuging on a large platinum cone, the salt was crystallised four times from platinum, and then the dry material was fused in platinum with the aid of a blast-lamp, the products of combustion being suitably deflected. The clear colourless salt was removed in lumps about the size of a pea and preserved in weighing bottles with well-fitting stoppers.

Sodium Bromide.—The purest bromide furnished by the J. T. Baker Chemical Company was used as the source of raw material. On careful examination it was found to be free of sulphates, phosphates, carbonates, bromates, and iodides, and to contain but a faint trace of chloride. A comparatively large amount of suspended iron was found. This was easily removed by filtration. The filtrate was colourless and free of iron. The sodium bromide from it was re-crystallised in platinum six times, each time with efficient centrifugal drainage. Examination at this point failed to reveal any chloride, and the colourless crystals were then re-crystallised eight more times from pure water. The salt was now regarded as pure.

It was fused in platinum, and while quite hot was removed from the crucible, and quickly placed in very warm dry weighing bottles. Absolutely clear colourless brilliant lumps of bromide, somewhat larger than the size of a pea, were obtained and preserved. The hygroscopic nature of sodium bromide necessitated this procedure, and the clarity of the lumps of bromide was an indication of its sufficiency.

Silver Nitrate.—The purest silver nitrate obtainable was re-crystallised three times in platinum. This was regarded as sufficient for nephelometric work, since values obtained by its use were solely relative.

Nitric Acid.—This was kindly furnished by Dr. W. H. Chapin, who had purified it for his work on the "Atomic Weight of Tantalum." It was entirely free of chlorides.

Ammonium Oxalate.—The colourless crystals of commerce were dissolved in pure water, and re-crystallised twice.

Ammonia Water.—Ordinary ammonia water was heated and the vapours absorbed in pure water.

Mercury.—Ordinary distilled mercury of commerce was thoroughly washed with potassium dichromate and sulphuric acid, then dried and doubly distilled in Hulett and

Minchin's glass distilling apparatus (*Phys. Review*, xxi., 388).

Preparation of the Silver Anode. In the previously published work on anion determinations with the double cup and silver anode, the anode was prepared by plating the gauze discs in a bath of $\text{KAg}(\text{CN})_2$ under a voltage of five and an ampère of one. The anode was then washed with water, dried, and gently heated, after which it was ready for a determination. Examination by the writer showed that with this procedure there was still some possibility of enclosed cyanide, and so the expedient of dipping the plated gauze in dilute HCl was tried. The HCl formed KCl, which was easily washed out with distilled water. The gauze was then heated to incipient redness, and was ready for weighing. Repeated tests showed no trace of soluble matter. The weighed anode could be immersed in boiling water, and re-ignited, without showing any loss in weight, and since after electrolysis the weight of the halogen is determined directly by difference, the above method of preparing the anode plate was obviously satisfactory. However, for the final work in this investigation, recourse was had to the double oxalate of silver and ammonia electrolyte. This was done only because the silver from such a bath was of a more porous character, and hence presented greater surface to the action of the ionic halogen during the electrolysis. The platinum gauze was made the cathode in the oxalate electrolyte, and with the use of a clean platinum rod as anode, a current of 1 ampère at 1.5 volts was sent through the solution. The gauze rotated at about 200 r.p.m. This low current admits of a close coherent coating on the platinum. It was then gradually increased to 4 ampères, and an extremely heavy porous deposit of silver finally obtained. The proper plating of the gauze requires constant attention for about five hours, because the gas bubbles evolved during the electrolysis collect on the gauzes, act as non-conducting cushions, and thus prevent an even coating. The gauze must therefore be lifted out of the bath from time to time in order to break the bubbles and hence ensure a satisfactory deposit. This deposit is then dipped in dilute HCl, and very thoroughly washed with pure water, after which it is heated in the Bunsen flame to incipient redness, cooled in a desiccator, and weighed. Repeated ignition with subsequent immersion in water showed no change in weight. This method of preparing the silver anode is therefore adequate.

Mode of Procedure.—Since pure fused chloride of sodium is perfectly stable, its weighing was a very simple matter. The lumps of salt for each determination were transferred from a weighing bottle into a small weighed beaker and the increase in weight of the latter observed, of course using an almost identical beaker for a counterpoise. The weighed beaker containing salt was then carried in a desiccator to the electrolytic cell.

Fused sodium bromide is, however, hygroscopic; and a variation in the above procedure was therefore adopted. The bromide was contained in an exceedingly well-ground weighing bottle, and was weighed against a similar bottle containing bromide. The stopper of the bottle was then removed, about the required amount of salt shaken out into a clean beaker, and the stopper replaced, after which the bottle was ready to be re-weighed, the decrease in its weight, of course, representing the apparent weight of the salt used. The operation of removal of salt never consumed over fifteen seconds, and the glass was handled through linen gloves. The construction of the stopper of the weighing bottle was such that there was no possibility of loss of bromide in transference. When clear fused masses of sodium bromide are exposed to the action of ordinary air for even forty five seconds, the surface becomes clouded and the transparency is lost. Investigation of the increase in weight of the hygroscopic bromide when exposed to the air in the balance case gave the following results:—Five grms. of bromide were carefully weighed in a closed weighing bottle, the stopper was then removed, and the increase in

weight noted. In one minute no increase was observed; in three minutes 0.03 mgrm.; in five minutes 0.06 mgrm.; in ten minutes 0.13 mgrm. It is quite obvious that in an actual determination there was no likelihood of error in the weight of the sodium bromide, because of the fifteen seconds or less during which the weighing bottle was open. Furthermore, each successive quantity of sodium bromide removed from the weighing bottle was as brilliant in appearance as the very first taken out.

All weighings were made by substitution. Since the counterpoise was always almost exactly similar to the object weighed, the weights required were never large in amount, and thus errors due to atmospheric conditions were greatly minimised. All weighings were, of course, reduced to a vacuum standard, with a consideration of density at 20°.

In the inner compartment of the double cup was placed the salt under analysis. The total dilution never exceeded 65 cc. The weighed silver-plated anode supported in the platinum-protected chuck of the motor shaft was placed centrally in the inner beaker. The lowest gauze was about 1 cm. above the surface of the mercury. About 5 cc. of a saturated aqueous solution of common salt was then put in the outer compartment, and this was diluted with water to about 200 cc. The circle of thin platinum wire was thus completely covered. The rod of platinum serving as cathode connected with the mercury was then put in position, and the cover glasses replaced. The anode was rotated at a speed of 200 r.p.m., and the current applied. Decomposition of the salt was instantly visible. The anode darkened because of silver halide. The sodium passed into the mercury as amalgam, and was decomposed in the outer cell. This oxidation was greatly facilitated by the introduction of the circle of platinum described, for, in reality, a secondary cell entirely independent of the main electrolytic circuit was established. In this, the elements were amalgam, platinum, and the solution of sodium chloride. The purpose of the sodium chloride introduced into the outer compartment is thus to act as a conducting medium at the beginning of the decomposition. Hydrogen bubbles "break" from the platinum wire in a continuous steady stream until the end of the electrolysis.

During the progress of the electrolysis the ampère gradually decreases because of the removal of salt from the inner cell. When the ammeter needle has fallen to below 0.03 ampère the current is interrupted. The anode is raised from the cell, is thoroughly washed with pure water, dried in this electric oven, cooled in a desiccator, and weighed. Treatment of the liquid remaining in the inner cup will be described later.

Previous analyses made in the double cup were of quantities of salt rarely exceeding 0.15 grm., and excellent results were obtained, if no decomposition of amalgam occurred in the inner cup. Quite evidently such decomposition would give rise to the formation of sodium hydroxide, which would undergo electrolysis with the consequent deposition of silver oxide on the anode. This contaminates the silver chloride, alone desired, and vitiates the value of the increase in weight of the anode. One cannot foretell just when decomposition of amalgam in the inner cup will or will not take place. Even working with the most scrupulous cleanliness does not necessarily ensure complete absence of decomposition in the inner cell, although under such conditions the secondary decomposition would be minimised. This secondary electrolysis is therefore possible and quite likely, and to this cause may, in part, be attributed irregular values occasionally obtained heretofore. Silver oxide, however, decomposes at 250° with the liberation of oxygen, whereas silver chloride is stable at a much higher temperature. Thus if the anode after electrolysis, containing AgCl contaminated with Ag₂O, be heated to above 250°, the oxide is decomposed, and the anode consists substantially of silver and silver chloride exactly as is desired. This condition was effectually brought about by recourse to the electric oven described

above. The temperature ranged from 330° to 400°, and was thus quite sufficient to decompose the oxide. It is noteworthy that the oxide appears on the anode only near the end of the electrolysis and after practically all of the sodium chloride has been decomposed. (Its decidedly brown tinge distinguishes it from the bluish black chloride). It is thus a superficial formation, and hence can be easily and completely decomposed. It is readily seen that with the use of the drying oven at elevated temperatures the old bugbear of concomitant oxide formation on the anode is entirely dispelled.

Quite naturally larger quantities than 0.1 grm. of material are necessary for atomic weight work, and on increasing this amount considerable difficulty was encountered. With the use of over a grm. of salt in solution, and an initial voltage of 3.5, the increasing resistance in the cell caused the pressure to rise of itself to 6.5 volts. Complete decomposition of the salt occurred, but a black scum invariably appeared on the surface of the liquid in the inner cup. This black scum was identical with small quantities of a loosely adherent deposit on the silver anode. Examination proved it to be oxide of silver. Quantitative determinations of halogen content under such conditions were, of course, absurd. Continued experimentation led to the adoption and maintenance of a low voltage as a means of preventing the formation of the loose oxide. A voltage of 3.5, kept constant throughout the electrolysis, ensured a perfectly adherent deposit. And still the values of halogen obtained were very low. Trial after trial was made with varying conditions, but with no apparent advance.

All this work was done with a "six-decker" platinum gauze especially devised to pick up larger quantities of anions. Examination of the silver plate under a lens led to the discovery of a non-uniform coating, indeed minute spaces of platinum were exposed. Here, then, might be a reason for the low values obtained. If platinum is made the anode in a solution of sodium chloride, some NaClO and NaClO₂ are formed, lost, and quantitative retention of halogen as halide is impossible. The nature of the six-gauzed anode used prevented the deposition of a thick adherent plate of silver. The wires of each gauze were too fine in diameter, the gauze was too fine in mesh, and the gauzes themselves were too close together. Thus, in attempting the plating of a very heavy deposit the meshes would be closed up, giving even less anodic surface, and defeating the original purpose of the many-disc electrode. A triple disc anode, made and prepared as described above, was finally adopted. The proper preparation of the silver anode is most essential to the success of each determination. At no time during the electrolysis must the anion be permitted to come in contact with the platinum. If only small amounts of halide are used, then a comparatively thin coating of silver suffices to retain all the halogen. But in the case of much larger quantities great care must be taken to procure a uniform silver plate of considerable thickness, so that as the chloride ion, for example, converts the surface silver to halide and works its way to the core of the deposit, there should be sufficient silver at all times to protect the platinum base. If the deposit is not uniformly thick, it is readily seen that at the places of this deposit the ionic halogen will soon meet the platinum, even though there be sufficient silver in bulk on the rest of the gauze; and when the platinum becomes the anode, then the very disturbing secondary formations arise. It is very likely that this phenomenon is the chief cause of uncertain values in anion estimations obtained occasionally by various investigators. Emphasis must be laid on the necessity of a satisfactory silver plate. In the present work a deposit of 10 to 15 grms. of silver generally obtained. The use of a pure silver anode is, of course, ideal. A three-disc pure silver anode, of the same dimensions as the platinum gauze anode, with sand-blasted and perforated surface, was later used for several determinations, and gave excellent satisfaction.

A peculiar phenomenon noted in the course of this work

was the appearance, after drying in the oven, of a dark purplish "sublimate" on the silver-plated rod of the platinum anode, at a place just below the upper limit of the silver coating. Continued heating of the anode showed no loss in weight. Indeed, direct ignition of the "sublimate" had no effect. Since constant weight was obtained, the first thought of a volatile chloride or sub-chloride of silver, had to be laid aside. It was then believed that the electrolyte was, to a slight degree, drawn up the anode rod by capillarity. This would explain the presence of the apparent sublimate which, on solution in potassium cyanide and re-precipitation by nitric acid, proved itself to be a chloride of silver. The expedient of forming a very coarse deposit of metallic silver immediately above the gauzes proved the correctness of the capillarity assumption. The spongy, though perfectly adherent, deposit really acted as a sponge, and prevented the electrolyte's creeping up the rod and eventually coming in contact with the platinum above.

Silver chloride is, to a slight degree, soluble in water, and so account must be taken of the silver chloride present in the inner-cup liquid after electrolysis. This was done by precipitation of the dissolved chloride with an excess of silver nitrate in the presence of nitric acid, and determination of the turbidity thus produced by means of a nephelometer (*Am. Chem. Journ.*, xxxi., 235). In addition to the dissolved silver chloride, there was also some sodium hydroxide, due to decomposition of amalgam in the inner cup. This had no effect on the nephelometric work, since the silver oxide formed when silver nitrate is added to the inner-cup solution is completely dissolved by the nitric acid added to catalyse the formation of the chloride opalescence. The determination of the silver chloride in solution was carried out as follows:—

A standard solution of pure sodium chloride was prepared by dissolving 0.0414 gm. NaCl in 250 cc. water. This was solution A. One cc. of it was equivalent to 0.0001 gm. Cl. Solution B, 250 cc. in volume, was then made by diluting 1 cc. of solution A with pure water. A solution of silver nitrate was prepared by dissolving 10 grms. silver nitrate in 250 cc. pure water. A 1:10 aqueous solution of nitric acid was likewise at hand.

The liquid remaining in the inner cup (never more than 70 cc. in vol.) was pipetted into a calibrated 250 cc. flask, and the inner cup was washed six times with small amounts of pure water, pipetting each washing into the flask. The original wash-waters obtained in washing the anode after removal from the inner cup were then added to the contents of the flask, and the whole made up to the mark with pure water. These 250 cc. therefore contained all the dissolved silver chloride, and since the volume was identical with that of solution B, a direct comparison of the halide content of the two solutions could be made. To this end, 1 cc. of the silver nitrate solution and 1 cc. of the nitric acid were added to each of two 6-inch test-tubes. One tube was then filled with the solution to be examined, the other with the solution B of known strength. The solutions were thoroughly agitated with clean glass rods, and placed in the nephelometer. Constant reading was had after a lapse of fifteen minutes. The ratios of the respective turbidities furnished a direct determination of the halide present in the test solution. For example, if the nephelometric ratio was 8 is to 4, i.e., the reading of the tube containing the standard was 8.0, whereas the reading of the test solution gave 4.0, then, according to the scale of the instrument, there was twice as much turbidity in the test as in the standard, and consequently twice as much halide.

Although the solubility of silver chloride in water varies, it is less than 2 mgrms. per litre, so that if the 65 cc. of solution in the inner cup were saturated with AgCl there could only be about 0.1 mgrm. of the salt in solution; hence an accuracy of only 10 per cent in the nephelometer would be quite sufficient for the purpose. However, the nephelometer admits of much greater precision, and hence permitted the following variation in the electrolytic

procedure. Instead of conducting an electrolysis to the complete analysis of the sodium chloride, the current was interrupted, while traces of undecomposed salt still remained, and these traces were nephelometrically determined, using the same procedure just described. It was a source of great satisfaction that, with the widely varying amounts of chloride determined by the nephelometer, the total halogen obtained gave uniform atomic weight figures. The identical method of nephelometric tests was used in the bromine estimations.

(To be continued).

WATER SUPPLY.*

By JOHN H. BALFOUR BROWNE, K.C., D.L.

(Concluded from p. 203).

IN case of spring waters, these are collected where they issue from the earth from their underground recesses in protected tanks, and from these the water, which, in many cases has been sufficiently filtered by Nature, is conveyed to the clear water tank as in the case of surface water. But when, as in the case of surface water, Nature does not produce a ready-made article, and the water is liable to surface pollution, then filtration is a necessity, and as in many other cases in this connection, our ancestors were wiser than they knew. Indeed, experience is often more valuable than science, and is universally the foundation upon which all safe science is built. Sand filters have been used in Britain since about 1829. These filters are tanks from 6 to 8 feet deep. Over the floor drain pipes or channels lead to the outlet pipe, and over these we lay a layer of broken stones and gravel. These stones are laid to a depth of 2 or 3 feet, the larger stones being at the bottom of the tanks, and the smaller bearing the 2 feet of sand which was supposed to be the filtering and purifying medium. The water is allowed to percolate downwards at a certain slow rate, and the effect is to remove mechanically certain matters in suspension. For many years our chemical experts saw little or no value in sand filtration, because in chemical analyses they found little or no difference between the filtered water and the unfiltered raw water. But it was left to bacteriologists to find the real significance of sand filtration. We know now that after use a jelly-like deposit is formed on the top of the sand, and that that film has prevented the water getting through the filters at the ordinary vertical rate of 4 to 6 inches an hour, or about 2½ million gallons a day per acre of sand. One ingenious engineer had the jelly scraped off the surface of his filter, and the water flowed more freely certainly, but there were within a few hours urgent telephonic messages from the bacteriological department announcing the arrival of thousands of bacillus coli, and that the water supplied by that company was not fit to drink. The fact is that it is the organic slime which is formed on the top of the sand, and which the sand is only useful in supporting, that is the effective agent in filtering the water, for the organic slime destroys the micro-organisms which are in impure water. It is in this respect that our ancestors in using their sand filters were wiser than they knew.

We know that Nature used to be thought red in tooth and claw, and no doubt lions and tigers and ravening wolves appeal to our trembling imaginations. But it is the still small animals that are the real danger. We are taught by science to tremble at the sight of the common house fly—the missionary of typhoid and diarrhoea; or the flea from a certain rat which inoculates the plague. But it is the micro-organisms, which are to be found in contaminated waters, and which are so readily distributed by our system of town supply, that are in fact the most dangerous foes of the human race. We have seen, how-

* A Discourse delivered before the Royal Institution, March 17, 1911.

ever, that Nature purifies our chalk waters, and also works with a will to save us pumping, but here again Nature by her bacteriological laboratory toils for the health of the human race. M. Duclaux has well said, "Whenever and wherever there is decomposition of organic matter, whether it be the case of a weed or an oak, of a worm or a whale, the work is exclusively performed by infinitely small organisms. They are the important, almost the only agents of universal hygiene; they clear away more quickly than the dogs of Constantinople or the wild beasts of the desert the remains of all that has had life, they protect the living against the dead. They do more; if there are still living beings, if since the hundreds of centuries the world has been inhabited life continues, it is to them we owe it." So, too, it comes about that while the micro-organisms which cause cholera, typhoid, and tubercle, which are so rapidly conveyed to us by means of water, and then exercise their fateful activities, which bring us disease and death—there are beneficent bacteria which "come to succour us who succour want," and these are applied as a bastion or a defence against our enemies by means of the at one time despised sand filter. I think it was Napoleon who said that a wise general should not fight too often with the same enemy, for the enemy was apt to learn too much from his implacable foe. We have fought often with the bacillus of cholera and typhoid, and have learned of our battles. Nothing could be more tragic in the way of instruction than what took place in Hamburg and Altona in 1892. Both Hamburg and Altona are dependent for their water supply on the Elbe, but the in-take for the Hamburg supply is above the town; the in-take for the Altona supply is below Hamburg, at a place below the point where the sewage of that town, with its 800,000 inhabitants, is discharged into the river. The Hamburg supply had, therefore, a great initial advantage over that of its neighbouring town. But the cholera epidemic scourged Hamburg, and the Angel of Death passed very lightly over Altona. In Hamburg the deaths from cholera amounted to 1250 in 100,000, and in Altona to only 221 per 100,000 of the population. Where the division between the two towns was only the imaginary line down the centre of a street, and the houses on one side of the street, being in Hamburg, were supplied with the above-town water, and the houses on the other side were supplied by the below-town water, the cholera visited with fatal results the houses on the Hamburg side, while those on the Altona side were free from the disease in this new Pass-over.

These haggard statistics are to be accounted for only by the fact that the foul sewage-polluted water of the Elbe which was supplied to Altona was carefully filtered, while the comparatively pure water taken above Hamburg for the supply of that town was not. Altona had the protection of the micro-organisms in its sand filters. Hamburg had no such protection, and suffered accordingly.

A similar experience in relation to another water-borne disease—typhoid—has been put on record by the Massachusetts Board of Health. There in twenty years, from 1856 to 1876, the death rate from typhoid in that State was 8.6 per 10,000 of population: in the years between 1876 and 1895, when private wells had been given up and a public supply of filtered water been substituted, the death rate was only 4.1 per 10,000, and between 1896 and 1899 the death rate went down to 2.6 per 10,000. The State Board report:—"The death rate from typhoid fever has generally fallen as the percentage of the population supplied with public water has risen, for the reason that the majority of the deaths from this disease have occurred among communities and portions of communities not supplied with public water."

But an examination of our own Thames water at Hampton showed there were 1644 micro-organisms in 20 drops of water, and the Thames water, after passing through the sand filters, was found to contain only 13 such organisms in the same number of drops. The discovery of the 1644 germs was at the time so startling that the shares

of one of the water companies dropped in value; and I think these 1600 did valiant duty in the arbitration which had to determine the value of the company's undertakings when they were being transferred to the Water Board.

But notwithstanding these startling vindications of sand filters, the great town of Chicago takes its water from Lake Michigan, which receives the untreated sewage of various towns having in the aggregate a population of over two million people, and has not thought it necessary to subject its water to any preliminary purification before distribution. That town has, however, with curious inconsistency, diverted its own sewage from the Lake, but it has undertaken that sanitary improvement only in connection with the commercial undertaking of the drainage and ship canal.

We know that one of the riddles of the politico-economic platform is "What is raw material, and what is a manufactured article?" But we have seen sufficient to see that "raw water" is quite a rare commodity, and that most of our waters are manufactured articles. Even Eastern countries like China and India have long "doctored" water with alum to get rid of clay by coagulation. But in this country not only do we get rid of the turpidity of water by sedimentation, but we purge the waters of micro-organisms, including pathogenic germs, by storing in large reservoirs as well as by filtration. Very hard waters, waters containing lime and magnesia, are treated and softened by what is called Clarke's process. Everyone knows that chalk waters fur boilers and kettles, and that the bicarbonate of lime is precipitated by boiling; but Clarke's process consists of a chemical method which expels chalk by chalk, and is an ingenious application of science to the practical purpose of softening water which lengthens the life of boilers and saves soap. But, again, water may be too soft. Hill waters are sometimes too soft to be palatable. Water at Keswick is under half a degree of hardness; Loch Katrine water, 1 degree; Thames and New River water is about 14 degrees.

But it is found that distilled water or soft lake or river water acts with extreme rapidity upon lead, and many cases of lead poisoning have occurred in consequence of persons drinking waters which have been in contact with the lead of which distributing pipes are, for the most part, constructed. It has been said that sand filters remove the lead, but at present it is the rule to treat, or "doctor," these very soft waters, as is done at Sheffield, where, to overcome this difficulty, from half to (rarely) three grains of powdered chalk is added to each gallon of water with excellent results. It has been found, too, that loam or clay remove by merely carrying down organic or inorganic impurities from water; and it is certain that the precipitation of lime which takes place in Clarke's process has some effect in the same direction, although, from experiments made by Dr. Percy Frankland in connection with the Cambridge Water Bill of 1910, it does not seem to be a thoroughly effective method of purification. In connection with that Bill, a suggestion was made that suspicious waters—waters drawn from wells in the chalk in close proximity to certain villages—could be made perfectly safe by the chlorinisation of water; and it was stated that the ozone process which has been adopted in relation to certain waters forming part of the supply to Paris is also a useful and protective process in cases where waters are liable to organic pollution, and in which the danger-signal of bacillus coli are found. These instances are sufficient to show that water to be potable must pass through the hands not only of the engineer with his filter and storage, but also through the hands of the chemist and bacteriologist; in fact, water, unlike the poet, is made, not born.

It is little more than a year ago that Paris was suffering from the drowning floods, which called, I think, for a Mansion House Relief Fund, and just before Christmas the south of Lincolnshire was under water, and the town of Newark stood out like an island in a sea which stretched twenty-five miles or nearly, from Nottingham on the one side to Collingham on the other. At the same time, after

the rains there was a leak in the artificial bank of the Glen, which caused the flooding of the whole of the Bourne Fen. The whole country was a sea, with a sad archipelago of villages and farms.

Here, then, there was enough of water flowing down from the hills of Derbyshire to spoil the prospects of a harvest, to ruin the potato crops of these fat fens, and in a few months from now we may hear, as we often do, of some great Lancastrian town having been put on the short commons of two hours a day for its water supply, and of its having only a small number of days' supply in its reservoirs. These two aspects of the rainfall surely call for some national action. As to the Fens, all that is suggested is the deepening of the rivers which take the waters to the sea. Within the last two years the Trent Navigation Company have taken 300,000 tons of material out of the River Trent, which, of course, has had the effect of modifying the floods to some small extent. But, of course, almost the whole of the lands in these districts have been won from the sea and are kept from the clutches of the sea, and land waters only by means of embankments and drains.

The creed of Socialism is that as no one made the land, or the minerals in the land, no one can be the owner of them, and the reverse of that curious coin is that labour makes all wealth; therefore, to labour all wealth belongs. But these gentlemen should see the lands of Lincolnshire, and they will discover that they have been as much created by the labour of men and the capital of owners as a steam-engine or a boat. But the lesson we should learn from these floods, I suggest, is not only that we must find a means of getting rid of land waters, which is poor economy in a country which, in parts, suffers at times from severe periodic droughts, but that we must come to some comprehensive conclusion as to a scheme by which, while training the fury of the floods of winter—by domesticating, as it were, our wild animal "water," and holding it in reservoirs—we may have such a deposit as will prevent floods, and tide us over periods of dry weather, and so make what is at present the "curse" of rains, the blessing of abundant water supply. This principle has been recognised in all our great impounding schemes, but it wants to be carried into higher politics, as an economic principle in relation to our water supply. But to do this effectively it must be done not on a parochial, but on a national scale. The importance of the management of water sources and of distribution upon a large scale is only now, it seems, beginning to dawn upon the obscurity of public opinion. In the early days water seemed to be everywhere, and even when that delusion had been routed by dry summers, the matter was still treated as a purely local question. A town was on a river, and it dipped into it. It was on a water-bearing strata and it sunk a well, but as I have shown by instances it is evident that the purely local treatment of the water question must be abandoned. Great towns, as we have seen, have gone to great distances and have appropriated areas which may, in the words of the Duke of Richmond's Commission of 1869, "naturally and geographically belong to districts nearer to such sources." And these enterprises have raised the large question which, as I said, is in a sense political—the question of national water. The importance of this larger treatment of the great subject first dawned upon the commercial instincts of men. Reservoirs were formed in many of the Yorkshire and Lancashire valleys in which the mill-owners banked, as it were, the winter floods to keep their wheels going in the summer droughts, and before the days of railways when canals were still real highways and not the peaceful sluggards of rural districts, where with the lazy bulging barge they form the easy subject of the sketcher's art. In those days when they were the sole highways of commerce, many reservoirs were formed in the hills to feed the canals with the water which was lost in lockage. Nothing could better illustrate the importance of "large maps" in relation to water supply than a passage from recent commercial history. During the last year the trade of our eastern

ports diminished. These ports are largely dependent on the trade of the Rhine, the Elbe, and the Weser, which with their important canal connections still form the important highways for the commerce of Germany. That falling off was accounted for mainly by the fact that the various Continental canals had been too scantily supplied with water, and people were surprised to find that that want of water was coincident with, and was in fact caused paradoxically by, the wetness of the summer. The explanation of the paradox is easy enough. These great waterways, some of which bear barges of 600 tons burden, are dependent for their water supplies not upon local rain-falls, but upon the great bank of Europe—the snows of the Alps, where, as in a reservoir, the winter's moisture is kept in a safe of ice until the summer with its heat melts the lock. But in the wet, cold, inclement summer the ordinary amount of melting had not taken place. The rivers ran low notwithstanding the rainfall, and commerce was impeded for want of water in these great ducts of trade. That fact should teach us the importance of larger views of the question than pettifoggers have been entertaining. Here is the commerce of Grimsby and Hull and Goole dependent upon the storing of the snows of the Jungfrau, and the height of the thermometer in Switzerland. We in England do not possess such a natural reservoir as the snows of the Alps, and must have recourse to other expedients if we are to do the best for this matter of water supply.

There is, at the present time, a good deal of sporadic information as to the water supplies and resources in various localities, and mining engineers have, from their experience, some knowledge of the subsoil or underground waters, for these, of course, are the enemy with which they have to contend in their operations, but there is no general survey to determine what are the supplies and what are the water resources of this country; there is no general knowledge as to the underground water supplies. We know that in many districts these are being pumped for supply, in many where mining is going on they are, with reckless economy, being pumped to waste. But what is required is a comprehensive knowledge both of the overground and underground reserve forces for water supply, and until that is prepared any legislation with regard to water supply must be merely hand to mouth, unscientific, and futile; and this seems to have been the wise opinion of Mr. Lithiby, of the Board of Trade, who gave evidence before the Joint Select Committee on the Water Supplies Protection Bill, which sat and reported during the last session of Parliament.

The necessity for the acquisition of such knowledge is emphasised by the proceedings and Report of the Royal Commission which has been inquiring and reporting upon canals and waterways since the year 1906. No one can say that the investigations of that Commission have not been exhaustive, although many may think that the Reservations of Lord Farrer and three other Commissioners seem to show that their labours will prove absolutely futile. But the Commission has gone further, and proposes to improve the waterways of England, and these great new or improved canals are to connect the Midlands and South Staffordshire with the estuaries of the Thames, the Humber, the Mersey, and the Severn. These four routes, which are, after all, only to be large barge canals, suited for barges of, in one scheme, 100 tons burden, and in another of 300 tons burden, are, in the Report, referred to as the "cross," and if this gigantic scheme is carried out at an expense, according to Sir John Woolfe Barry's estimate, of, for the small scheme, £13,393,483, or for the large scheme of £24,513,823, certainly England would be financially crucified. But criticism of that imaginative proposal forms no part of my present purpose. It is only interesting to me to note that after the Commission had adumbrated this idea, and ascertained approximately the cost of constructing the "cross," which, as I have said, would be a cross greater than England could bear, they bethought themselves how they were to get water for their canals—

in the deplorable absence of the Alps—and they instructed an engineer to survey and inquire and to give them an estimate of the cost of getting the water. I have no doubt he did his work as well as he could. He found ready to his hand the admirable statistics as to rainfall which are collected by Dr. Mills, but complains, rightly enough, that "other questions connected with the national water supplies appear to receive less attention." Of course, it is quite an exception to find anywhere river gaugings, and the engineer in question says:—"This inquiry has shown the necessity, if such problems as those which the following Reports attempt to solve are to be thoroughly investigated in future, of some public authority being charged with the duty of recording the flow of rivers, and of the proportion of the rainfall available or run off in catchment basins overlying different geological strata in various parts of the country."

But this claim to water for canals which, according to the reporter, would involve an expenditure of £1,194,000, without including the cost of obtaining the power or the cost of water compensation, and which is, of course, in addition to the sums estimated for construction by Sir John Wolfe Barry, raises again in an acute form the whole question of our national supplies, and points to the absolute necessity now of some systematic dealing with this great question. The nation is being forestalled by municipalities, and here is a suggestion that a Canal Board should lay a gigantic hand upon some of our sources of supply. The time for dealing with the matter is *now*; but, as in other cases, it is quite likely that the matter will be postponed until it is "too late." Indeed, in many directions, those last tragic words of Gordon at Khartoum seem to be adopted as the motto of England.

We all know that the British pride themselves on being a practical people. But we often believe ourselves to be possessed of virtues we have not got. One of the best indications of the practical ability of the English people as a nation is to be found in connection with legislation. When a matter begins to stir the minds of the public, the politicians invariably think that postponement is the best policy, and, acting upon this principle, they appoint a Royal Commission, a Departmental Committee, or a Joint Select Committee of the two Houses, and after that the matter is never heard of again. There are more questions buried in blue books than bodies in the catacombs. The Committee or Commission thinks it is furthering the great purpose of reform, and it makes a Report, and the sound dies away and silence resumes her disturbed possession. As you will understand, the question of water supply was just one which would be interred with the bones of a Royal Commission. The matter has been in the minds of restive people, who really are like the angels of the Pool of Bethesda, and stir the waters of healing—for many years. There was a Royal Commission on water supply in 1869, which saw that there were large questions involved. There was also a somewhat similar recommendation in the Report of the Select Committee on the Public Health Act 1875 Amendment Act in 1878. Nothing has resulted from these recommendations, but the introduction of some dead letter clauses into the Manchester, the Liverpool, the Birmingham, and the Birkenhead Acts. But the recommendation was, in effect, a recognition of the necessity of considering the needs of districts, and a more comprehensive treatment of the whole subject.

The Sewage Commission's Third Report contains a statement of the Commissioners that "in our opinion a properly equipped authority is essential, and we unhesitatingly recommend the creation of such an authority." That recommendation was made in 1903 (Report, para. 44), and I need scarcely say nothing has come of it. There was recently introduced into Parliament a somewhat crude measure called "The Water Supplies Protection Bill," which sought to alter the law of underground waters to endow landowners with rights to waters which were not in defined streams which they do not at present possess, and a few other trifles of legislation. The Bill

was referred to a Joint Select Committee, and the inquiry was useful and instructive. The Report for the most part gave the go-by to the fads of the measure, but the Committee took an exceedingly sensible view in relation to the great question of National Water Supply. They reported on the desirability of conserving in all reasonable ways the water supply of the country. They recommended "the creation of an organisation empowered to inquire into the whole question of surface and underground water supplies from a comprehensive standpoint, to supervise the future allocation of supplies, and to serve as an authoritative adviser of Parliament in the consideration of particular schemes." This was such a reasonable proposal that I have no hesitation in predicting for it the oblivion such proposals mostly achieve.

But this Committee, not deterred by the wrecks of other reports which lie along the whole shore of legislation, went on to say that there was "an urgent need for a survey at once comprehensive and in detail of the water supplies and water needs of the country, and for the adoption of measures for conserving the supply and disposing of it to the best advantage."

This, again, seems a dictate of common sense, and will probably be disregarded by any government which is in, or comes into power, for governments naturally look more to the conserving and disposing of votes than of waters, even although it seems certain that in the past we have, like a spendthrift nation, been playing ducks and drakes with our water capital. Here I find myself in eager agreement with that parliamentary voice crying in the wilderness of contemporary politics. I know, however, that it is not in the graveyard of the lobbies, but in the streets of public opinion, that reforms are inaugurated and pushed forward. It is because there is a real Referendum to public opinion—and because public opinion makes an echo which reverberates futilely for a time in St. Stephen's, but when the diapason becomes loud enough makes itself heard even in these lethargic quarters which think not of the necessities of the nation, but of the loaves and fishes of office—that I thought it worth while to appeal to you to-night upon this great matter of our national water supply.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Imperial College of Science and Technology,
Royal College of Science, South Kensington, London, S.W.,
October 4th, 1911.

GENTLEMEN,—I beg to forward you the Annual Report of the International Committee on Atomic Weights for 1912, to which I have appended, as desired by them, the signatures of Professors Clarke, Ostwald, and Urbain.

Slight changes have been made in the atomic weights of calcium, erbium, iron, mercury, tantalum, and vanadium, which are indicated, in accordance with a suggestion received from Germany, by asterisks.

The only addition to the list of elements is that of niton (radium emanation), with the symbol Nt. and the atomic weight 222.4 as determined by Gray and Ramsay. This is in fair agreement with the value calculated by Debierne from observations on the rate of the flow of the gas.—I have the honour to be, Gentlemen, your obedient servant,

T. E. THORPE.

To the Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

Report of the International Committee on Atomic Weights,
1912.

Since the report of the Committee for 1911 was prepared, a number of important determinations of atomic weight have been published, which may be summarised as follows:—

Nitrogen.—Guye and Drouguine (*Journ. Chim. Phys.*, 1910, viii., 473), from seven analyses of N_2O_4 , find, in mean, $N = 14.010$.

Sulphur.—Burt and Usher (*Proc. Roy. Soc.*, 1911, A, lxxxv., 82), by analysis of nitrogen sulphide, N_4S_4 , have determined the ratios $S:N :: 1.0:0.43687$. Hence, calculating with $N = 14.009$, $S = 32.067$, in good agreement with the accepted value.

Chlorine.—Burt and Gray (*CHEMICAL NEWS*, 1911, ciii., 161 and 170) have continued their work upon the density of hydrochloric acid, and confirmed their former determination of $Cl = 35.46$.

Iodine.—Baxter (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1591) has re-determined the ratio of iodine to silver with extreme care. Combining his results with the previously determined ratio of silver to iodine pentoxide, he finds $Ag = 107.864$ and $I = 126.913$. The value for silver varies from that found by Richards and Willard, and the discrepancy is as yet unexplained.

Sodium.—Goldbaum (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 35) has made analyses of sodium chloride and bromide by a new electrolytic method. The salts were electrolysed with a mercury anode and a weighed silver cathode, and on the latter the halogen was collected in weighable form. From the chloride, with $Cl = 35.458$, Goldbaum found $Na = 22.997$; the bromide, with $Br = 79.920$, gave $Na = 22.998$.

Calcium.—Two papers by Richards and Hönigschmid (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1577; 1911, xxxiii., 28) on the atomic weight of calcium have appeared. From analyses of calcium bromide, $Ca = 40.070$, when $Ag = 107.88$. From analyses of the chloride, $Ca = 40.074$. The value 40.07 is adopted in the table accompanying this report.

Cadmium.—Perdue and Hulett (*Journ. Phys. Chem.*, 1911, xv., 155; see also Richards, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 888), from electrolytic analyses of cadmium sulphate, conclude that the atomic weight of cadmium is near 112.30. This is lower than the accepted value, but as the investigation is being continued with other salts of cadmium, any change in the table should be deferred.

Mercury.—Easley (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1117) has continued his work on the atomic weight of mercury, varying his methods. New analyses of the chloride give $Hg = 200.63$, in confirmation of his former determinations. In a private communication he states that analyses of the bromide lead to the same value. The new figure, $Hg = 200.6$, should be adopted.

Vanadium.—McAdam (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1603), by reducing sodium vanadate to sodium chloride, by heating in a stream of dry hydrochloric acid, finds $V = 50.967$, or 51 in round numbers. The latter figure is as probable as any.

Tantalum.—Balke (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1127), by hydrolysis of tantalum pentachloride, has determined the ratio $2TaCl_5 : Ta_2O_5$. The mean of five concordant determinations gives $Ta = 181.52$, when $Cl = 35.46$. The rounded-off value 181.5 should be accepted.

Tellurium.—Flint (*Am. Journ. Sci.*, 1910, [4], xxx., 209) has continued the work reported by Browning and Flint in 1909 on the fractionation of tellurium by hydrolysis of the tetrachloride. With successive fractions the atomic weight steadily decreased. Seven analyses of the basic nitrate representing the tenth fractionation gave values for Te ranging from 124.25 to 124.42. As the work is still in progress, any acceptance of these low figures would be premature.

Iron.—Baxter, Thorvaldson, and Cobb (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 319), from analyses of ferrous

International Atomic Weights. (1912).

Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium*	Ca	40.07
Carbon	C	12.00
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.5
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium*	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	3.99
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron*	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.10
Lithium	Li	6.94
Lutecium	Lu	174.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury*	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton* (radium emanation)	Nt	22.4
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.6
Radium	Ra	226.4
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.07
Tantalum*	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.4
Thulium	Tm	168.5
Tin	Sn	119.0
Titanium	Ti	48.1

		O = 16.
Tungsten	W	184·0
Uranium	U	238·5
Vanadium*	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

bromide, find $\text{Fe} = 55·838$ when $\text{Ag} = 107·88$. In another communication (*Ibid.*, p. 337), Baxter and Thorvaldson find $\text{Fe} = 55·836$. The latter figure is the mean of two series, meteoric iron being taken as the starting-point. The value $55·84$ is given in the table.

Uranium.—Gehsner de Coninck (*Comptes Rendus*, 1911, clii., 711 and 1179), by reduction of UO_2Cl_2 and $\text{UO}_3\cdot\text{H}_2\text{O}$ to UO_2 in hydrogen, concludes that $\text{U} = 238·5$. The work is only approximate in character.

Scandium.—Meyer and Winter (*Zeit. Anorg. Chem.*, 1910, lxxvii., 398), in a preliminary series of experiments, find values for Sc ranging from $44·86$ to $45·37$; in mean, $45·12$. This is higher than the recognised value, but its adoption would be premature. More details are needed.

Neodymium.—By extended and careful analyses of the chloride, Baxter and Chapin (*Proc. Am. Acad.*, xlii., 215) have re-determined the atomic weight of neodymium. From the ratio $\text{NdCl}_3 : 3\text{Ag}$, $\text{Nd} = 144·268$. From the ratio $\text{NdCl}_3 : 3\text{AgCl}$, $\text{Nd} = 144·272$. A small correction raises the value to $144·275$. The rounded-off value $144·3$, given in the table, may be properly retained.

Erbium.—Hofmann (*Ber.*, 1910, xliii., 2635), from analyses and syntheses of the sulphate of "neocerium," finds $\text{Er} = 167·68$. This may be rounded to $167·7$.

Argon.—Determinations of the density of argon, by Fischer and Froboese (*Ber.*, 1911, xlv., 92), give a mean value of $19·95$. Hence $\text{A} = 39·90$.

Nitron.—Gray and Ramsay (*Proc. Roy. Soc.*, 1910, A, lxxxiv., 536), with the aid of the micro-balance, have determined the density of the gaseous emanation from radium, to which they give the name *nitron*. The mean value found gives $\text{Nt} = 223$, but the value $222·4$ is preferred (compare also Debiere, *Comptes Rendus*, 1910, ci., 1740). The gas is a member of the argon group, and seems to be entitled to recognition in the table.

The table of atomic weights for 1912 is given. In accordance with a suggestion received from Germany, the changed values are indicated by an asterisk. The changes are few in number, and only in two cases are they large.

F. W. CLARKE.
W. OSTWALD.
T. E. THORPE.
G. URBAIN.

INSTITUTE OF CHEMISTRY.

THE Council of the Institute of Chemistry have inaugurated a series of Lectures, the first of which was delivered by Mr. BERTRAM BLOUNT, F.I.C., at King's College on Thursday, October 26th.

In the unavoidable absence of the President, Dr. Beilby, the Chair was taken by Prof. J. MILLAR THOMSON, LL.D., F.R.S., who opened the proceedings with a reference to the scheme of lectures, which, he said, was an extension of the work of the Institute on lines mainly directed to benefit advanced students of chemistry. Its aim would be to indicate the scope and object of the work actually carried out in various branches of professional chemical practice, as distinct from academic training; while occasionally the lectures would deal with matters of forensic and ethical interest. Except for one or two lectures delivered in its early history, the Institute had not assumed in any way the functions of a teaching body, though the Charter provided for such functions. The relations between teachers of

chemistry and other professional chemists had been made closer in recent years mainly owing to the high standard of scientific ability attained by so many who devoted themselves to the chemistry of every day life and of industrial processes. The Council thought it would be a good thing if younger chemists were brought into touch with the actual practitioners as men whose experience had revealed the directions for future developments. The President in his addresses had shown that when a University undertook the professional training of physicians and surgeons they fully realised the difference between the academic and professional scientific training. The training in medicine, he said, was based on preliminary training in science, but from an early stage it was moulded and guided into practical channels by men who were actually themselves engaged in the practice of their profession. Apart from the great value of the information which could be imparted by men of standing and experience, the mental contact with them and the new views of practical and intellectual proportion and perspective which would result, would be of inestimable value to the students.

Prof. THOMSON then welcomed the Institute to King's College, and called upon Mr. Blount to deliver his lecture, the first of two on "Cement," of which the following is a brief abstract.

The Lecturer limited his discourse to the consideration of calcareous cements as being of predominant importance, and more particularly to the Portland cement industry, the size of which may be judged by the fact that the world's production is estimated at 25,000,000 tons per annum, valued roughly at £35,000,000. The industry is essentially a chemical one, and in the interests of both manufacturer and consumer is, and should be, controlled by the chemist.

The earliest form of calcareous cement is probably calcium sulphate sufficiently dehydrated to form plaster of Paris. Its disadvantages lie in its lack of plasticity and its liability to attack by water. On the other hand, calcareous cements, properly so-called, while being plastic, are capable of hardening and are resistant to water. The common fallacy that the setting of lime mortar is due to the action of lime on the sand with which it is mixed was once more exploded by the lecturer. It has long been known that some siliceous materials have an advantage over others as aggregate for mortar. These are known generally as "pozzolanas," and their usefulness depends on the fact that they contain hydrated silica or attackable silicates which interact with lime and form compounds more or less resistant to the action of water. Similarly it has been known that some limestones are better than others in providing strong and resistant lime for mortar. There seems to be no record that limestones were deliberately and intelligently chosen for the hydraulic quality of the lime which they furnished until the time of Smeaton, who, in considering with what material he should build the Eddystone Lighthouse, ascertained that Aberthaw limestone was undoubtedly hydraulic, and, desiring to know why, applied to Mr. Cookworthy, a chemist of the period, whose office as consultant was creditably fulfilled. It was found that those limestones which were most hydraulic contained the largest proportion of argillaceous material. But, not content with this, he reasoned that this quality might be improved by the addition of what was then known to be capable of conferring hydraulic properties on ordinary lime, and accordingly used Trass, a pozzolanic material.

From the subject of hydraulic limes the lecturer went on to discuss the manufacture of so-called "Roman Cement," a crude form of Portland cement made by burning lumps of clayey limestone. The foundations were thus being laid of one of the largest chemical industries in the world. Starting with the notion of imitating Roman cement, the progenitors of the Portland cement industry arrived at the idea that when chalk and clay were mixed and burned an hydraulic material was produced which, when ground, would set and form a strong sound cement. The function of the chemist who concerns himself with

this industry was dealt with at some length. When a new works is to be started, there has to be considered the nature and available quantity of the raw materials, the accessibility of a supply of fuel, the suitability of the proposed site, the choice of process and the appropriate plant, and such matters of transport, supply of labour, and probable markets, which go far to determine the commercial success of any undertaking. The function of the chemist continues after the works are started, and on him depends the smooth control of the quality of the cement produced.

In the next lecture, to be given in the latter part of November, the Chemistry, properly so-called, and Testing of Cement will be dealt with. The lectures will be published.

NOTICES OF BOOKS.

Practical Chemistry for Medical Students. By ALEXANDER CHARLES CUMMING, D.Sc. Edinburgh: James Thin. 1911.

A GOOD preliminary course of practical chemistry suitable for medical students is outlined in this book. In it are described the preparation of some common gases and simple salts, the investigation of the properties of gases, common acids, alkalis, and elements, a short course of volumetric work and qualitative analysis for the common metals and radicles. Separations are not included. Some organic compounds are dealt with, and a short section is devoted to methods of identifying simple organic substances. In all the practical work described in the book should require an attendance of about sixty hours in the laboratory, and the student who works through it should gain some familiarity with simple manipulations and methods of practical chemistry, and an acquaintance with the general properties of the common reagents. In addition he should have acquired a grasp of the main principles of qualitative analysis. It seems probable that the book might be found useful for other than medical students. The generalisations of methods given in it are an excellent feature, and every effort is made to induce the student to think about his work and not to do it mechanically.

Matriculation Directory. No. 59. September, 1911. London: University Tutorial Press. (1s. net).

THE Matriculation Directory contains abstracts of the regulations of the University of London examinations, both for matriculation and the higher examinations in Arts and Science, and full information is also given about the classes of the University Correspondence College, which continues to do successful work and to achieve excellent results. The Directory contains reprints of the majority of the papers set in the September examination together with criticisms and solutions of them, and intending candidates will find that the model answers will give them many valuable hints, and are well worth the most careful study.

CORRESPONDENCE.

PURIFYING MERCURY IN THE LABORATORY.

To the Editor of the Chemical News.

SIR,—I have just read Mr. Bryant's letter on this subject in your issue of the 15th ult. I cannot say whether the contrivance is widely known, but it has certainly been long known. I used it regularly (in the form Mr. Bryant himself describes, with a drawn-out funnel tube) more than thirty years ago in the laboratory of the College of Science here (now Armstrong College), and had then no idea that it was new. New or old, it is very efficient.—I am, &c.,

J. T. DUNN.

Newcastle-on-Tyne, October 24, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other is expressed.

Zeitschrift für Anorganische Chemie.
Vol. lxxii., No. 1, 1911.

Melting-point of Minerals in the Light of Recent Researches with the Gas Thermometer.—Arthur L. Day and Robert B. Sosman.—The authors have previously described a method of determining temperatures up to 1550° with a maximum error of about 2°. Using this method they have found the following melting-points:—Zinc, 418.2°; antimony, 629.2°; silver, 960.0°; gold, 1062.4°; copper, 1082.6°; palladium, 1549°; platinum, 1755°.

Influence of Pressure on the Melting-point of some Metals.—John Johnston and L. H. Adams.—The metal was placed in a graphite crucible in a steel bomb, and heated in a small electrical resistance furnace; the temperature was measured by means of a thermoelement. As soon as the required pressure was reached the solidification-point of the metal was determined by reading off the thermometer every half minute. It was found that the melting-point is a linear function of the pressure; it rises with increasing pressure in the case of lead, cadmium, and tin, and with decreasing pressure in the case of bismuth.

Definite Compounds with varying Composition of the Solid Phase.—W. J. Smirnow and N. S. Kurnakow.—The authors give general types of the conductivity and hardness diagrams for definite chemical compounds with varying composition of the solid phase. The study of the conductivity shows that all substances which are formed in the system magnesium silver have a varying composition of the solid phase. A minimum occurs in the hardness diagram corresponding to the argentide, MgAg.

Colour of Iodine Solutions.—H. Ley and K. v. Engelhardt.—A solution of iodine in ethyl alcohol has a broad absorption band with a maximum at $1/\lambda = 2150$, and a minimum absorption occurs at $1/\lambda = 2850$. Solutions of iodine in hexane and chloroform show a maximum absorption at about $1/\lambda = 2000$, and indications of a faint absorption band at 3500. An ethereal solution of iodine takes up an intermediate position between the brown alcoholic solution and the violet chloroform and hexane solutions.

Uranium Hexafluoride.—Otto Ruff and Alfred Heinzelmann.—Uranium hexafluoride is formed when fluorine or hydrofluoric acid acts on uranium pentachloride, the tetrafluoride being made simultaneously. The hexafluoride is also obtained when fluorine acts on uranium or uranium carbide in presence of a small amount of chlorine. It is a yellowish crystalline substance which boils under atmospheric pressure at 55°, but melts at 69.5°, its vapour pressure being then about 2 atmospheres. The vapour density of uranium hexafluoride is 11.7 at 448, and the vapour contains the heaviest gas molecule yet known. Tetrachlorethane, carbon tetrachloride, chloroform, and nitrobenzene all dissolve the hexafluoride. It is a very active substance, readily decomposing to give the tetrafluoride. It is very hygroscopic, and is rapidly decomposed by water.

Rate of Hydration of Metaphosphoric Acid.—D. Balareff.—The rate of the transposition of metaphosphoric acid into the ortho-acid, $\text{HPO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4$, is proportional to the concentration, and hydration is not catalytically accelerated by H-ions but by metaphosphoric acid itself. The author is now engaged in determining the conductivity of aqueous HPO_3 solutions.

Preparation of Pure Potassium Ferrocyanide.—Karl Schröder.—Potassium ferrocyanide crystallises from hot saturated solutions with 3 molecules of water. When the water in a specimen is to be determined indirectly the

surface of the salt must be as limited as possible because of its tendency to oxidise. The best way to determine the iron in potassium ferrocyanide is to decompose the salt with concentrated sulphuric acid and use Baudisch's "cupferron" (nitrosophenylhydroxylaminammonium). The ferrocyanide can also be decomposed with HgCl_2 in aqueous solution, and then titrated with KMnO_4 .

Equilibria with Lead Carbonate Precipitates.—W. Herz.—The author determined the equilibria with lead carbonate precipitates by shaking a lead salt (sulphate, chloride, bromide) with sodium carbonate solution of known strength at 25° , and titrating the excess of sodium carbonate. The following are the results obtained:—

$$\frac{[\text{Na}_2\text{CO}_3]}{[\text{NaBr}]_2} = 3.5 \times 10^{-4} \text{ to } 2.7 \times 10^{-4},$$

$$\frac{[\text{Na}_2\text{CO}_3]}{[\text{NaCl}]_2} = 1.2 \times 10^{-4} \text{ to } 1.0 \times 10^{-4},$$

$$\frac{[\text{Na}_2\text{CO}_3]}{[\text{Na}_2\text{SO}_4]} = 1.2 \times 10^{-2} \text{ to } 1.0 \times 10^{-2},$$

$$\frac{[\text{PbCO}_3]}{[\text{PbSO}_4]} = 0.08.$$

MISCELLANEOUS.

Faraday Society.—A Special Meeting will be held on Wednesday, November 8th, 1911, at 8 p.m., at the Institution of Electrical Engineers, Victoria Embankment, W.C. (near Waterloo Bridge), when Dr. E. G. Acheson, of Niagara Falls, will give an account of his researches to the members of the Society. The address will be accompanied by experiments. Non-members will be admitted by ticket, to be obtained on application to the Secretary, 82, Victoria Street, Westminster, S.W.

Literary Intelligence.—Messrs. Chatto and Windus are publishing immediately a very important work on the Cancer Problem, entitled "The Enzyme Treatment of Cancer." The book, which is written by John Beard, D.Sc., explains the author's theory of the origin and nature of cancer, and contains not only a definite statement of the enzyme treatment, but particulars of a well authenticated case in which the treatment has been used with complete success. Dr. Beard is a scientist of many years experience and patient investigation, and his book is a serious attempt to deal with the gravest problem with which medical men are faced.

Association of Teachers in Technical Institutions.—The Annual Meeting of the Association of Teachers in Technical Institutions will be held at the Borough Polytechnic, Borough Road, S.E., on Saturday, November 4th, the President, Mr. Barker North, in the Chair. The annual report of the Council, which will be considered at this meeting, deals with the large increase in the membership of the Association in the past year, and with active work during that period. Branches have been formed in Ireland and Wales, so that the activities of the Association now spread over the whole kingdom. After the consideration of the report, a discussion will be initiated at 4 p.m. on the Board of Education Examinations in Science, by Mr. C. F. Smith, Manchester School of Technology, and Mr. J. Wilson, Battersea Polytechnic. To this discussion visitors are invited. Particulars can be obtained from the Hon. Secretary, Mr. P. Abbott, the Polytechnic, Regent Street, W.

Royal Institute of Public Health.—Berlin Congress, 1912. —The Council of the Royal Institute of Public Health have accepted an invitation from the Ober Burgomeister (the Lord Mayor) of Berlin to hold their Congress in 1912 in that City, from Thursday, July 25th, to Sunday, July 28th inclusive, and a Local General Arrangements Committee has been formed consisting of representatives of the

Royal Ministry of the Interior, the Imperial Board of Health, the City of Berlin, the Medical Officers of the Head-Quarter Staffs of the Army and Navy, the University of Berlin, the Medical and Hygienic Societies of Berlin, &c., to promote the success of the Meeting. The Congress will be under the Presidency of the Right Hon. the Earl Beauchamp, K.C.M.G., LL.D., His Majesty's First Commissioner of Works, and will be conducted in the following Sections:—

- A. *State Medicine.*—President: Sir T. Clifford Allbutt, K.C.B., M.D., LL.D., D.Sc., F.R.S., Regius Professor of Medicine in the University of Cambridge.
- B. *Bacteriology and Comparative Pathology.*—President: Prof. G. Sims Woodhead, M.A., M.D., LL.D., F.R.S.Ed., Professor of Pathology in the University of Cambridge.
- C. *Child Study and School Hygiene.*—President: Sir James Crichton-Browne, M.D., D.Sc., LL.D., F.R.S., Lord Chancellor's Visitor in Lunacy.
- D. *Military, Colonial, and Naval.*—President: Major Sir Ronald Ross, K.C.B., M.D., D.Sc., F.R.S., Professor of Tropical Medicine in the University of Liverpool.
- E. *Municipal Engineering, Architecture, and Town Planning.*—President: P. C. Cowan, D.Sc., M.Inst.C.E., Chief Engineer of the Local Government Board, Ireland.

The various Congress and Sectional Officers will also include gentlemen of German nationality occupying distinguished Scientific and Municipal positions. Facilities will also be afforded for visiting the various Public Health and Educational Institutions in Berlin, &c., in connection with the Imperial Board of Health, the Municipality, the University, &c., and it is confidently hoped that the Congress and the unique opportunities which will thus be given to representatives of Municipalities, County Councils, and other Sanitary Authorities of the United Kingdom for becoming practically acquainted with Institutions in the work of which they are concerned, will not only be of much interest but of the greatest value. Arrangements are being made for travelling and hotel accommodation at reduced charges. The subscription for each Delegate is one guinea.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Chemical Industry, 8. "Deflocculation (as affecting Lubrication)," by Dr. E. G. Acheson.

ROYAL INSTITUTION, 5. General Monthly Meeting.
WEDNESDAY, 8th.—Faraday Society, 8. (Special Meeting). Address by Dr. E. G. Acheson, of Niagara Falls.

THURSDAY, 9th.—Royal Society. "The Spectrum of Boron," by Sir A. Crookes. "A Chemically Active Modification of Nitrogen produced by the Electric Discharge," by Hon. R. J. Strutt. "Production of Solid Oxygen by the Evaporation of the Liquid," by Sir J. Dewar. "Gaseous condensable Compound, Explosive at Low Temperatures, produced from Carbon Disulphide Vapour by the Action of the Silent Electric Discharge," by Sir I. Dewar and Dr. H. O. Jones. "Optical Dispersion—a Comparison of the Maxima of Absorption and Selective Reflection for certain Substances" and "Influence of the Solvent on the Position of Absorption Bands in Solutions," by Dr. T. H. Havelock. "An Experimental Investigation of Gibbs' Thermodynamical Theory of Interfacial Concentration in the Case of an Air-water Interface," by P. G. Donnan and J. T. Barker.

FRIDAY, 10th.—Physical, 5. (At Finsbury Technical College). "Reflecting Polariscopes for the Study of Optical Stress in Materials," by S. P. Thompson and E. G. Coker. "Effects of Holes and Semicircular Notches in the Distribution of Stress in Tension Members" (demonstrated by Polarised Light), by E. G. Coker. "A Surface Tension Phenomenon," "Temperature Rise in Drops as they Part," and "Temperatures of Equidensity of Liquids," by C. R. Darling. Exhibition of a large Harmonograph, "Physiological Effect of an Alternating Magnetic Field," Demonstrations of Acoustical Experiments (New and Old), by S. P. Thompson.

THE CHEMICAL NEWS.

VOL. CIV., NO. 2711.

CHARACTERISTICS AND CHEMICAL COMPOSITION OF SOME EARLY MATCHES.

By EDWY GODWIN CLAYTON, F.C.S., F.I.C.

THE author has examined specimens of various early matches, including some of the original "lucifers," which contained no phosphorus, but ignited by friction when drawn through a piece of folded sand-paper tightly compressed by the finger and thumb.

The first commercially successful friction matches were of this type, and were made during the years 1826-27 by John Walker, a chemist and apothecary, of Stockton-on-Tees. But he did not call his matches "lucifers." Competitors soon afterwards supplied matches, similar to Walker's "friction-lights," under the designation of "lucifer matches" or "lucifers" (a trade name which, from contemporary literature, the author has found to have been invented by Samuel Jones, of the Strand, London, a vendor of light-producing and other appliances). The name of "lucifer" came to be applied in common speech to wooden-stemmed matches differing very greatly from the original lucifers, and even now is sometimes used, especially by workmen.

The original "lucifer" matches were followed in the early thirties by "Congreves." These contained phosphorus, and were inflamed by being "struck on the box," or by friction upon a rubbing surface attached to it. How the use of the name "Congreve" arose is uncertain. Probably some maker named his goods after Sir W. Congreve, whose war-rockets a few years previously had been the talk of Europe. The question is still being investigated by the author, and will be dealt with in the article "Matches," to appear in vol. ii. of the forthcoming edition of "Thorpe's Dictionary of Applied Chemistry."

Before Walker introduced his "friction-lights," various devices belonging to the class of "chemical matches," such as Heurtner's "Eupyrion" (mentioned in Faraday's "Chemical Manipulation"), and the "Prometheans" of the before-mentioned Jones (alluded to by Darwin in the "Voyage of a Naturalist"), together with the semi-savage steel and tinder-box, were the only means of obtaining fire in general use.

The author has not been able to investigate chemically a specimen of Walker's matches, which are extremely rare, but the matches placed at his disposal by friends comprised specimens (almost equally rare) of English and French "lucifers" (date 1832-33), similar to Walker's friction-lights; of Jones's "Prometheans" (date 1828-29), one of the most successful forms of the "chemical match"; of six kinds of "Congreves" (dates ranging from 1835 to 1850), phosphoric, ignitable by friction, and of German manufacture; of Viennese cigar-lighters (1850); and of some Austrian matches of later but uncertain date. The rubbing composition upon a "Congreve" box was also examined.

The two specimens of *lucifer matches* (1832-33), made by British and French manufacturers respectively, possessed dark grey rough-looking heads, the sulphur-dipped sticks or splints being of chip-wood, flat and rectangular. The splints of the English matches were more neatly cut than the French, and in appearance and size the first-named very closely resembled Walker's friction-lights, a specimen of which the author has had an opportunity of inspecting. Walker's splints were not sulphur-coated. In composition, the "lucifers" approximated to Walker's matches, the heads of which, according to various writers, contained sulphide of antimony, potassium chlorate, and

gum. The same constituents, with free sulphur, were found in the "lucifers." In each case was present also a small quantity of ferric oxide: possibly due to the use of an impure antimony sulphide. Analysis of the dry material of the heads gave the following results:—

Class—Lucifer Matches.

	English lucifer matches (R. Bell and Co.), Date, 1832-3.	French lucifer matches. Date, 1832-3.
Antimony sulphide ..	24.6	18.1
Sulphur	6.5	12.5
Potassium chlorate ..	27.6	41.0
Ferric oxide.	5.6	3.5
Gum	35.7	24.9
	100.0	100.0

The "Prometheans" (for which the author is indebted to Mr. H. H. Hammond) were part of the contents of one of the only six existing boxes known to Mr. Edward Bidwell, a great authority on early means of producing fire or obtaining a light, and owner of a remarkable collection of appliances for the purpose. Prometheans consisted of slightly tapering spiral rolls of paper, enclosing at the broader end about a decigram. of igniting composition, in the middle of which was embedded, not a glass bulb, as is usually stated, but a minute fusiform glass tube partially filled with sulphuric acid, coloured and somewhat diluted. Accompanying is a sketch of one of these tubes, greatly enlarged (Fig. 1). The actual size did not exceed

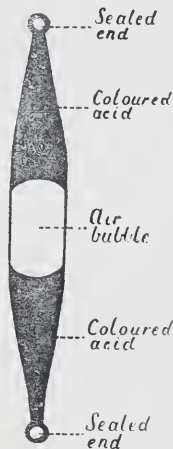


FIG. 1.—TUBE OF COLOURED ACID FROM ONE OF JONES'S "PROMETHEANS."

7 mm. in length, and 1 mm. in breadth at the widest part. In the sketch the sealed ends of the tube are unshaded, and the unshaded oval in the middle denotes an air-bubble, present in each tube investigated. A blue liquid fills the rest of the tube. Prometheans were supplied in double-lidded ornamental leather-covered cases, or in similar Japan-lacquered metal boxes, together with two pairs of pliers, held in position by a clip in the outer lid. When the match was held by one pair, and the head nipped by the other, or if the head were bitten (Darwin, *loc. cit.*), inflammation occurred, owing to contact being established between the acid and the chlorate mixture, by fracture of the little tube. The igniting composition hitherto has been described, more or less inaccurately, as containing sugar, fulminate, &c., in conjunction with potassium chlorate, but it will be seen that the constituents were found to be sulphur, lycopodium, potassium chlorate, and gum only. There was no sugar, and no other component

than those stated could be discovered. The liquid in the tube was diluted sulphuric acid, tinted by indigo. The figures of the analysis were:—

Class—Chemical Matches (Prometheans).

Igniting composition—

Sulphur	21.7
Lycopodium	8.8
Potassium chlorate	31.9
Gum	31.6
	100.0

Liquid in glass tube—

Sulphuric acid (H ₂ SO ₄)	61.9
Water	38.1
Indigo	minute amount
	100.0

The "Congreve" matches presented little variation in composition. All, with one doubtful exception, were of Continental manufacture, although in most cases the labels were in English. Usually only the initials of the makers' names were given. "B.F. in S." was probably Bernard Fürth, of Schuttenhofen, Austria. There was great variety in appearance and quality. For instance, the "Best London Congreves" (No. 1) and "J. C. K.'s matches" (No. 2) were miserable products, with badly cut sticks and irregular shapeless heads. Link's "Chemische Streichteuerzeuge" (No. 3) were better, with fairly neat square splints and medium-sized greyish blue heads. "I. N. E.'s." (No. 4), neatly cut square-sticked matches, with well-shaped reddish brown heads, might have been turned out of a twentieth century factory; and the other matches (No. 5) by the same maker, with circular sectioned splints and very small dark blue tips (at the extreme end of the stick) were comely enough. These

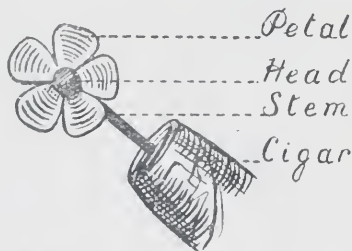


FIG. 2.—A. N. POLLAK'S "D'BLEAML'N" CIGARREN ZÜNDER.

matches were in the original oval chip-wood box, with a reddish brown rubbing composition (No. 6) on the bottom and on the lid. Enough were at disposal to enable the author to try how they ignited. Though above sixty years old they inflamed easily when struck upon the rubbers. "B.F. in S.'s" (No. 7) matches (also well made) had very minute pear-shaped drab coloured heads, on unusually thin circular sticks. The Austrian matches (No. 8), of later date, maker unknown, differed from the rest in being joined together at the base. The heads were brown, small, and of less diameter than the square splints. A. N. Pollak's cigar-lighters (No. 9) consisted of purple dyed, 1.5 cm. long, wooden stems, with large red or yellow heads, forming the centres of variously dyed five-petalled canvas or buckram flowers, affixed to the stems, which were to be inserted in the end of a cigar before the heads were "struck" (Fig. 2). The petals and stalks were impregnated with nitre, which was present also in the heads. These "D'Bleaml'n" were readily and fiercely inflammable.

For the specimens examined the author is indebted to Messrs. E. Bidwell, H. H. Hammond, V. B. Crowther-Beynon, F.S.A., Fred. G. Somerville, and J. T. Cater. Especial thanks are due to Mr. Bidwell, also, for interesting information upon fire-producing appliances of many kinds. And for help in various other ways, in connection with his study of the subject, the author is obliged to Mr. Henry H. Williams, Mr. Frank C. Marchant, and Mr. F. G. Somerville (before-mentioned).

23, Holborn Viaduct, E.C.

NOTE ON THE DETERMINATION OF NICKEL.

By F. IBBOTSON, B.Met., B.Sc., A.R.C.Sc.I.

BRUNCK'S method for the determination of nickel by precipitation with dimethylglyoxime from an ammoniacal solution (*Zeit. für Angew. Chem.*, 1907, xx., 834) has deservedly come into general use in metallurgical analysis. It has been applied to the analysis of nickel steels by Bogoluboff (*Stahl u. Eisen*, 1910, 458), Wdowiczewski (*Stahl u. Eisen*, 1908, 960), Iwanicki (*Stahl u. Eisen*, 1908, 1546), and others, and Spring (*CHEMICAL NEWS*, civ., 58) uses it in the analysis of German silver.

As the nickel compound sublimes at 250° C., most operators, after washing with hot water, dry at or about 100° C., and weigh. This procedure possesses the advantage that the weight of the precipitate is nearly five times that of its contained nickel, but it is open to the objection that towards the end of the washing the precipitate exhibits a decided tendency to pass through the filter, and it is doubtful, moreover, whether it is absolutely insoluble in hot water.

Bogoluboff has proved that the precipitate may be safely ignited to nickel oxide without loss, if the filter is first carefully charred without causing it to take fire, the temperature being then gradually raised to full redness. The author has repeatedly confirmed this observation, and uses this method of dealing with the precipitate, which makes it permissible to add ammonium nitrate to the wash water and obviate the difficulty mentioned above.

Spring's method for the analysis of German silver has been in use in these laboratories for a considerable time with excellent results. It suffices sometimes, however, to determine the nickel contents only of this alloy, and this can be done without previously separating the copper by the following method. Dissolve half a gram. of the drillings in 10 cc. nitric acid (1:20) and dilute to about 400 cc. with water. Add 2 or 3 decigrams. of tartaric acid to prevent the precipitation of the small quantity of iron almost invariably present, and then add ammonia in excess. Heat to about 50° C., add an excess of the dimethylglyoxime reagent, and after allowing to stand in a warm place for a few minutes, with occasional stirring, collect the voluminous precipitate on a filter-paper, or preferably on paper pulp. Wash with hot water containing ammonium nitrate till the washings are perfectly colourless. If the precipitate is then ignited as described below, the nickel oxide will contain small amounts of copper oxide, making the calculated nickel percentage from 1 to 1.5 per cent too great. Dissolve from the pulp, therefore, in a warm mixture of equal volumes of 1:20 nitric acid and water, wash well, and repeat the precipitation, filtration, &c.

Enclose the precipitate completely whilst still wet in two filter-papers, transfer to a crucible, and heat cautiously at the mouth of the muffle or over a small flame until the outer papers are thoroughly charred. Increase the temperature gradually and finish the ignition at a bright red heat.

The Metallurgical Department,
Sheffield University.

A DETERMINATION OF THE RATIO BETWEEN CHLORINE AND BROMINE AND SODIUM.*

By JACOB S. GOLDBAUM.

(Concluded from p. 215).

ALL electrolyses heretofore made with the double cup were conducted in the presence of sunlight or artificial yellow light, and no effort was put forth to prevent the coloration of the silver halide as formed. It seemed desirable in the present work to carry out several analyses of sodium chloride, and of sodium bromide, in a dark room, and to note any variation in effect. Three experiments were accordingly made at night, in complete darkness, except for the occasional use of a red lamp to illuminate the measuring instruments. The dried anode, holding supposedly pure undecomposed silver halide, was then weighed in red light. Reference to the table of results shows the difference in weight to be inappreciable. The photochemical change of silver halide is, perhaps, insignificant in this work because of the large excess of silver present with the silver salt. In any case, the comparative values obtained indicate the use of ordinary light to be quite safe.

In three electrolyses of sodium chloride conducted especially for the purpose, the liquid in the inner cup, after the current had fallen to 0.05 A, was examined for hypochlorites and chlorates. None was found in any tests. The halogen seemed to be present as halide only. The absence of a significant amount of silver from the electrolyte by solution of the silver anode is consequently proved. For in all the electrolyses only absolutely clear solutions prevailed, and the amount of silver ions in the presence of the excess of chloride must have been extremely small. The maximum solubility of silver chloride in water at 20° is 1.06×10^{-5} mols. per litre, hence its solubility product in mols. per litre is 1.12×10^{-10} . In determination No. 9, for example, the chlorine found by the nephelometer was 0.00026 gm. Since the volume in which this was contained was 50 cc., the chlorine concentration in mols. per litre was 1.5×10^{-4} . The amount of silver ions present in a clear chloride solution of such concentration cannot exceed 1.12×10^{-10} divided by 1.5×10^{-4} , or 0.75×10^{-6} mols. per litre, or 0.35×10^{-5} grms. of silver in 50 cc. (the volume of the liquid in the inner cup).

Moreover, the same lot of mercury was used as cathode in all the determinations. This was distilled until only a small residue remained. The residue was carefully examined for silver. A nephelometric test revealed the presence of 0.0003 gm. of the metal. Since this was the total quantity of silver transferred in more than fifty analyses of salt, it is quite evident that the effect of transference of silver from anode to cathode in a single electrolysis is negligible.

The matter of occlusion of salt solution in the constantly increasing deposit on the anode was of vital importance, and required careful consideration. It seemed quite possible, especially in the concentrated solution that obtained in the beginning of each electrolysis, for the silver halide in its formation to enclose minute quantities of the surrounding liquor; and although the mechanically enclosed water might probably be driven off by drying in the oven, the occluded sodium halide would exert its detrimental effect on the weight of the anode, and consequently vitiate the method for accurate work. The following experiments were therefore carried out: The dried anode after electrolysis was immersed in pure water saturated with distilled ammonia. Solution of the silver chloride resulted, and the anode was thoroughly washed with the ammonia water. Any occluded sodium chloride would be in the ammoniacal solution. On the addition of pure HNO_3 and on boiling, silver chloride was precipitated,

but only the chloride ion of the original silver chloride would be affected; any sodium chloride originally occluded would be in the filtrate. (Of course, the usual precautions in filtering silver chloride were observed). This filtrate was made up to definite volume, and its turbidity (extremely slight) determined by the nephelometer. This gave the zero-point, so to speak, and to the solution was then added an excess of silver nitrate; a nephelometric reading was taken, and the increase in turbidity noted. In three separate instances the maximum opalescence produced did not exceed 0.005 mgrm., an entirely negligible quantity, indicating quite definitely the absence of occluded chloride. Richards and Wells have conclusively demonstrated that occlusion of mother-liquor in precipitates is a function of the concentration of the medium in which the precipitation occurs. Acting on this, in two electrolyses only very dilute solutions obtained; that is, the salt was added in small quantities from time to time, where the fall of the ammeter needle indicated that only minute amounts of salt were undergoing analysis. There was, in these atomic weight values, no significant variation from those resulting on electrolysis of more concentrated solutions, thus again pointing to the absence of salt occlusions.

In three cases the anode, after the usual drying in the oven, was placed in a previously ignited and weighed porcelain evaporating dish, and heated by a protected Bunsen flame until complete fusion of the silver halide resulted. Cooling and re-weighing the dish and anode with a suitable counterpoise gave substantially the same values. In two determinations the loss in weight was 0.02 mgrm., while in the third the balance detected no change in weight. This procedure dispelled the thought of permanent retention of water in the dried deposit, and demonstrated the efficacy of the ordinarily employed method of drying the anode. Moreover, the concordance in values obtained by the use of widely different amounts of salt, strengthens the basic thesis that the increase in weight of the anode represents only the halogen content of the salt under analysis.

While waiting for the arrival of the triple gauze anodes a preliminary series of determinations was made with the ordinary double gauze electrode. In all other respects, the apparatus and materials were identical for both series of values. Greater concordance in the final series is to be ascribed to the use of larger quantities of salt as well as to more experience in the manipulation of the method.

The atomic weight of sodium, as given by the International Committee on Atomic Weights for 1910, was taken as 23.00.

In calculating vacuum corrections the following table was used:—

	Density at 20°.	Correction for 1 gm. of substance at 20°, 760 mm.
NaCl	2.14	+0.000418
NaBr	3.1	+0.000244
Ag	10.49	+0.000029
AgCl	5.56	+0.000073
AgBr	6.39	+0.000046
Brass weights ..	8.4	—

Weight of 1 cc. of air = 0.0012 gm.

By calculating from the approximate amount of halogen present the silver necessary to combine with it, the necessary vacuum correction for silver and silver halide was obtained, since only that weight of the anode actually undergoing change is to be considered in applying the vacuum correction. Thus, the approximate weight of chlorine times 3.04 gives the weight of silver actually attacked, and the correction is made for this and not for the whole anode.

The data for one single determination will be given in detail, to illustrate the mode of procedure. Subsequent record will be made of only the final figures necessary to establish the ratio of sodium to halogen.

* From the *Journal of the American Chemical Society*, xxxiii., No. 1.

PRELIMINARY SERIES.

No. of determination.	NaCl taken, in grm.	Cl found on anode.	Sodium Chloride,		At. wt. of chlorine. Na=23.00.	At. wt. of sodium Cl=35.458.(a)
			Cl determined in nephelometer.	Cl total.		
1.	0.81495	0.49423	0.00009	0.49432	35.460	—
2.	0.79370	0.48128	0.00007	0.48135	35.445	—
3.	0.88940	0.53952	0.00010	0.53962	35.483	—
4.	0.45642	0.27666	0.00013	0.27679	35.441	—
5.	0.43884	0.26612	0.00006	0.26618	35.458	—
6.	0.44239	0.26818	0.00010	0.26828	35.440	—
7.	0.64942	0.39381	0.00006	0.39387	35.449	—
8.	0.53706	0.32535	0.00046	0.32581	35.473	—

Average 35.456 $\pm$ 0.0037

FINAL SERIES.

Sodium Chloride.

9.	1.02234	0.61988	0.00026	0.62014	35.463	22.997
10.	1.02221	0.61957	0.00049	0.62006	35.463	22.997
11.	2.43474	1.47654	0.00038	1.47692	35.466	22.996
12.	1.46370	0.88780	0.00009	0.88789	35.466	22.995
13.	0.56934	0.34522	0.00012	0.34534	35.460	22.999
14.	1.00793	0.61103	0.00038	0.61141	35.465	22.995
15.	1.06501	0.64579	0.00021	0.64600	35.459	22.999
16.	2.16720	1.31442	0.00018	1.31460	35.463	22.997
17.	2.75219	1.66904	0.00035	1.66939	35.460	22.999
18.	0.92900	0.56337	0.00012	0.56349	35.458	23.000
19.	1.83527	1.11294	0.00030	1.11324	35.562	22.998

Average 35.462
 $\pm$ 0.000522.997
 $\pm$ 0.0003

Sodium Bromide.

No. of determination.	NaBr taken, in grms.	Br found on anode	Br determined in nephelometer.	Br total.	At. wt. of bromine. Na=23.00.	At. wt. of sodium. Br=79.920.(a)
20.	1.05343	0.81775	0.00028	0.81803	79.927	22.998
21.	1.33360	1.03542	0.00019	1.03561	79.932	22.997
22.	1.05652	1.51875	0.00061	1.51936	79.936	22.995
23.	5.02976	3.90513	0.00073	3.90586	79.930	22.997
24.	2.09332	1.62545	0.00009	1.62554	79.925	22.998
25.	6.46697	5.02162	0.00016	5.02178	79.920	23.000
26.	5.54733	4.30740	0.00028	4.30768	79.923	22.999
27.	7.03901	5.46575	0.00031	5.46606	79.926	22.999

Average 79.927
 $\pm$ 0.001422.998
 $\pm$ 0.0003

(a) F. W. Clarke, "A Re-calculation of the Atomic Weights."

Weighing of Sodium Chloride.

0.070 grm. = weights on pan excess over counterpoise.
+ 0.00085 grm. = rider reading.0.07085 grm. = total weights used.
+ 0.00003 grm. = correction for weights used.

0.07088 grm. = apparent excess weight of empty beaker over counterpoise

1.079 grms. = weights on pan excess over counterpoise.
- 0.00062 grm. = rider reading.1.07838 grms. = total weights used.
+ 0.00001 grm. = correction for weights used.1.07839 grms. = apparent excess weight of beaker and NaCl over counterpoise.
- 0.07088 grm. = apparent excess weight of beaker over counterpoise.1.00751 grms. = apparent weight of NaCl.
+ 0.00042 grm. = vacuum correction.1.00793 grms. = correct weight of NaCl.
0.61 grm. = approximate weight of Cl present in NaCl taken.0.61 $\times$ 3.04 = 1.85 grms. = approximate weight of silver combined with chlorine.

0.61 + 1.85 = 2.46 grms. = approximate weight of silver chloride formed.

1.85 $\times$ - 0.00003 = vacuum correction for silver = - 0.00006 grm.2.46 $\times$ 0.000073 = vacuum correction for silver chloride = 0.00018 grm.

Weighing of Anode.

3.150 grms. = weights on pan in excess of counterpoise anode.

+ 0.00024 grm. = rider reading.

3.15024 grms. = total weights used.
+ 0.00010 grm. = correction for weights.

3.15034 grms. = apparent excess weight of silver anode over counterpoise.

- 0.00006 grm. = vacuum correction for silver attacked.

3.15028 grms. = corrected excess of anode over counterpoise.

3'760 grms = weight on pan in excess of counterpoise anode.
+ 0'00097 gm. = rider reading.
3'76097 grms. = total weights used.
+ 0'00016 gm. = correction for weights.
3'76113 grms. = apparent excess weight of silver chloride anode over counterpoise.
+ 0'00018 gm. = vacuum correction for silver chloride formed.
3'76131 grms. = corrected excess of anode over counterpoise.
- 3'15028 grms. = corrected excess of anode over counterpoise.
0'61103 gm. = correct weight of chlorine found on anode.

Nephelometer Readings.

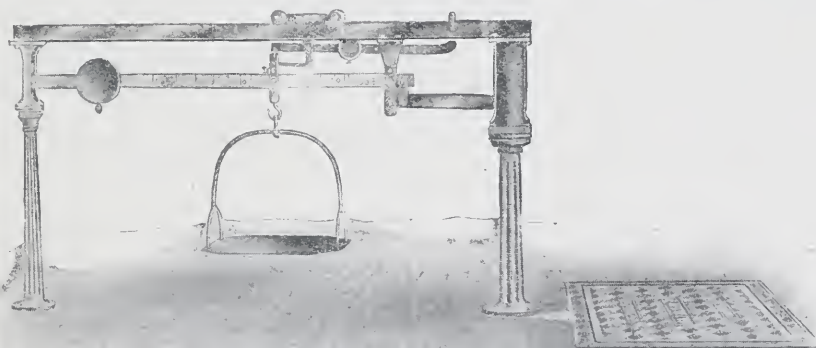
Standard.	Test.	Ratio.
5'0	1'9	3'80
7'8	3'0	3'84
9'1	3'5	3'84

Correction for chloride in solution = 0'00038 gm. chlorine.

Electrical Readings.

	Beginning of electrolysis.					End of electrolysis.
Voltage ..	3·5	—	3·5	—	3·5	— 3·5
Ampère ..	0·91	—	0·52	—	0·22	— 0·12
Time ..	9·8	—	9·20	—	9·45	— 10·15
						— 10·46

(Hence 1 hour, 38 minutes).



0'61103 gm. Cl found on anode.
+ 0'00038 gm. Cl determined as nephelometer.

0'61141 gm. total chlorine found.
1'00793 grms. NaCl taken.

1'00793 : 0'61141 = 23'00 + X : X. X = atomic weight of chlorine.

X = (23'00) (0'61141) / 1'00793 - 0'61141.
X = 35'465.

Determinations 10, 12, and 24 were carried out in darkness as mentioned above. After drying and weighing as usual, the halides on anodes in determinations 9, 11, and 20 were fused as previously described. No significant change of weight was observed. In determinations 17, 18, 19, and 27 the pure silver disc anode was used.

Since the above article was published in separate form as a thesis, Dr. W. A. Noyes has called attention to the

fact that the work is really a determination of the ratios between sodium and chlorine and sodium and bromine. The accepted value for the atomic weight of sodium, 23'00, is based on oxygen through either silver or chlorine, or bromine, and hence, as a piece of atomic weight work, the value of sodium is to be calculated. This was accordingly done, and with the results given in the last column of the table. The value of chlorine was taken as 35'158, of bromine 79'920 (F. W. Clarke, *loc. cit.*).

SPECIAL MACHINE FOR QUICKLY AND ACCURATELY COMPUTING THE PERCENTAGES OF MATERIALS COMPRISING A MIXTURE.

THE absolute necessity of mixtures containing the accurate and desired materials in the requisite percentage of each ingredient cannot be overestimated, and any machine which will expedite the operations of weighing must be of value to the manufacturer.

The machine illustrated is of the ordinary platform type, and mixtures can be made up in any desired percentage by simply balancing the steelyard. The percentages vary according to the requirement.

The barrow or container is placed on the platform, and is tared by the poise on the larger steelyard.

The bucket or whatever it is desired shall contain the second mixture is then tared on the smaller steelyard, and the runner is moved along until it rests on the percentage graduation which it is desired the second ingredient shall

bear to the *unknown* quantity, which has been placed on the platform.

When the amount placed in the smaller skip balances the steelyard, the desired percentage can be added to the bulk without any fear that it does not bear its correct proportion, thus avoiding all possibility of errors in calculating.

The machine is arranged with a platform measuring 48 in. by 30 in., and is capable of weighing up to a maximum capacity of 3 cwt.

It will readily be understood that machines of this character, which have been designed and manufactured by W. and T. Avery, Limited, of London and Birmingham, can be readily adapted to any ordinary requirement in various trades.

Physical Society's Annual Exhibition.—This Exhibition will be held on Tuesday, December 19th, and will be open both in the afternoon and evening.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions*.

193. "*Indicators of the Methyl-red Type*." By HUBERT HOWARD and FRANK GEO. POPE. (*Trans.*, 1911, 1333).

Azo-compounds of the methyl-red type were prepared by combining diazotised anthranilic acid with α -naphthylamine, dimethyl α -naphthylamine, diphenylamine, and phenyl- α -naphthylamine. Contrary to the statement of Tizard (*Trans.*, 1910, xcvi., 2485), the potassium salt of methyl-red can be obtained in a crystalline form, and is not deliquescent.

193. "*Dihydrocinnamenylcarbimide (8-Phenylethyl isocyanate)*." By MARTIN ONSLOW FORSTER and HERMANN STÖTTER. (*Trans.*, 1911, 1337).

Dihydrocinnamenylcarbimide, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}:\text{C}:\text{O}$, and some of its derivatives were studied, and in the course of their examination it was noticed that whilst this isocyanate converts menthol into the corresponding carbamate, cinnamenylcarbimide transforms that alcohol into menthyl carbamate, a change which involves the disappearance of phenylacetylene.

194. "*The Synthesis of Histidine*." By FRANK LEE PYMAN. (*Trans.*, 1911, 1386).

A preliminary account of the synthesis of *r*-histidine has already appeared (*Proc.*, xxvii., p. 92). The synthesis of histidine itself, that is, the naturally-occurring *levo*-modification of this base, has now been completed by the resolution of *r*-histidine.

Both the *d*- and *l*-varieties have been obtained in a practically pure state by crystallisation of the hydrogen tartrates.

195. "*The Action of Benzylamine on s-Dibromosuccinic Acid*." By EDWARD PERCY FRANKLAND. (*Trans.*, 1911, 1775).

When benzylamine reacts with *s*-dibromosuccinic acid in alcoholic solution it gives rise successively to the following compounds:—(I.) the *dibenzylamine* salt of dibromosuccinic acid; (II.) the *monobenzylamine* salt of bromomaleic acid; (III.) the *monobenzylamine* salt of *benzylaminobromosuccinic acid*,



and (IV.) the *monobenzylamine* salt of *dibenzylaminosuccinic acid*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_5)\cdot\text{CO}_2\text{H}$, from which the free acid can be obtained by dissolving in hydrochloric acid and precipitating with water.

When the reaction is carried out in aqueous solution the products isolated are the *dibenzylamine* salt of *dibenzylaminosuccinic acid* and the *dibenzylamide* of *i*-tartaric acid. This formation of an amide in aqueous solution is to be accounted for by an intramolecular rearrangement demonstrated by Lutz (*Diss.*, Rostock) in the action of ammonia and other amines on monohalogen succinic acids, whereby amides of malic acid are produced.

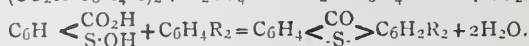
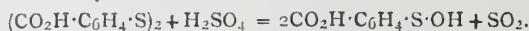
196. "*A Method of Determining Carbon and Nitrogen in Organic Compounds*." By EDWARD PERCY FRANKLAND. (*Trans.*, 1911, 1783).

The Frankland-Armstrong vacuum combustion process (*Journ. Chem. Soc.*, 1868, xxi., 77) can be adapted for the estimation of carbon and nitrogen in organic compounds. The gases (carbon dioxide and nitrogen) evolved during the combustion of a known weight of substance, generally 0.1 grm. or less, are collected, and measured over mercury in a graduated vessel; the carbon dioxide is then absorbed with aqueous potassium hydroxide, and the residual nitrogen transferred to a narrower graduated tube and measured over water.

The process can be carried out in less time than is required by the ordinary carbon-hydrogen combustion method, and the figures obtained both for nitrogen and carbon in a variety of organic compounds are in good agreement with theory. The presence of bromine in the molecule, even up to 80 per cent, has not been found to affect the accuracy of the results, hence this method appears to be of especial advantage in connection with organic substances containing both nitrogen and halogen.

197. "*The Synthesis of Derivatives of Thioxanthone from Aromatic Disulphides*." By EFFIE GWENDOLINE MARSDEN and SAMUEL SMILES. (*Trans.*, 1911, 1353).

The synthesis of thioxanthones may be accomplished by heating di-*o*-thiobenzoic acid or its derivatives with a suitable aromatic compound in presence of concentrated sulphuric acid, the interaction which takes place being summed up as follows:—



The method may be modified by arranging that the carboxyl group is present in the simple aromatic compound instead of in the disulphide; thus on heating *p*-dithiodimethylaniline with *m*-hydroxybenzoic acid and sulphuric acid, the corresponding thioxanthone is formed.

198. "*Trialkylammonium Nitrites and Nitrites of the Bases of the Pyridine and Quinoline Series*." Part II. By PANCHANAN NEOGI. (*Trans.*, 1911, 1598).

Picolinium nitrite is obtained, together with the nitrate, by concentrating an ice-cold solution in a vacuum desiccator. *Quinolinium nitrite* exists in solution, but not in the solid condition. *Piperidinium nitrite* has been obtained in colourless plates. *Pyridine methonitrite* is a reddish yellow liquid. *Piperidine methonitrite* crystallises in colourless plates. *Picoline methonitrite* forms red crystals, and *quinoline methonitrite* dark red crystals.

199. "*The Density of Liquid Sucrose and of its Solutions in Water*." By FREDERIK SCHWERS. (*Trans.*, 1911, 1478).

By melting sucrose under paraffin the author has succeeded in determining the density of liquid sucrose at temperatures between -15° and 115° .

The densities of aqueous solutions of sucrose containing 10, 20, 30, 40, 50, 60, and 70 per cent of sucrose have also been determined.

200. "*The Condensation of Crotonaldehyde*." By IDA SMEDLEY. (*Trans.*, 1911, 1627).

The condensation of crotonaldehyde under the influence of alkaline condensing agents has been studied. By oxidising the condensation product with silver oxide, and subsequently reducing with phosphorus and hydriodic acid, *n*-octoic acid has been identified. The γ -carbon atom of one crotonaldehyde molecule must therefore have reacted with the aldehyde group of a second molecule.

201. "*Ionisation in Non-aqueous Solvents*." Part I. By HARRY MEDFORTH DAWSON and MAY SYBIL LESLIE. (*Trans.*, 1911, 1601).

Measurements of the electric conductivity of non-aqueous solutions of alkali metal iodides and the corresponding polyiodides have shown that, in general, the polyiodides are ionised to a greater extent than the simple iodides. In methyl and ethyl acetate solutions the observed conductivity differences are very large, and in the latter solvent the polyiodides of potassium conduct from twenty-five to fifty times as well as the simple iodide. Evidence has been obtained in favour of the formation of definite polyiodides in such solutions, and the conductivity differences must be ascribed to differences in the degree of ionisation of the dissolved electrolyte. The simple alkali iodides would appear to be abnormally weak electrolytes when dissolved in methyl and ethyl acetates.

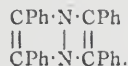
202. "The Formation of Glyoxalines from Acyl Derivatives of α -Keto- β -anilino- α -3-diphenylethane." By ARTHUR ERNEST EVEREST and HAMILTON MCCOMBIE. (*Trans.*, 1911, 1740).

Glyoxalines can be prepared from acyl derivatives of α -keto- β -anilino- α -3-diphenylethane by heating these compounds in sealed tubes with aqueous ammonia:—



From the benzoyl, acetyl, and formyl derivatives respectively there have been prepared by this method 1:2:4:5-tetraphenylglyoxaline, 1:4:5-triphenyl-2-methylglyoxaline, and 1:4:5-triphenylglyoxaline. The hydrochlorides, picrates, and platinichlorides of these substances have also been prepared.

In the formation of all these glyoxalines there was obtained, in varying quantities, 2:3:5:6-tetraphenylpyrazine:—



Some curious colour changes of α -keto- β -anilino- α -3-diphenylethane and its acyl derivatives have been noticed in the course of this work. α -Keto- β -anilino- α -3-diphenylethane itself is yellow, and gives a yellow solution in alcohol, but this solution becomes colourless on the addition of a drop of acid. The acyl derivatives, on the other hand, are colourless, and yield colourless solutions, but these solutions become strongly yellow on the addition of a drop of alkali. The probability is that there exist ketonic and enolic modifications of these substances.

203. "The Osmotic Pressure and Conductivity of Aqueous Solutions of Congo-red, and on Reversible Membrane-equilibria." By FREDERICK GEORGE DONNAN and ALBERT BUCKLEY HARRIS. (*Trans.*, 1911, 1554).

Measurements of osmotic pressure and electrical conductivity show that, although aqueous solutions of Congo-red are very considerably ionised, they exhibit an osmotic pressure corresponding very closely with the value calculated for single undissociated molecules. On dialysis, solutions of Congo-red suffer a gradual "membrane-hydrolysis." Constant values of osmotic pressure can only be obtained in presence of small concentrations of alkali hydroxide. The effect of various concentrations of sodium hydroxide and sodium chloride on the osmotic pressure has been studied. It has been shown experimentally and theoretically that a non-dialysing electrolyte such as Congo-red causes an unequal distribution of sodium chloride on either side of the membrane (in this case, parchment paper).

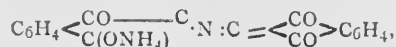
204. "Triketohydrindene Hydrate. Part V. The Analogues of Uramil and Purpuric Acid." By SIEGFRIED RUHEMANN. (*Trans.*, 1911, 1486).

Diketohydrindamine, $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{CH}\cdot\text{NH}_2$, which is formed by the reduction of oximinodiketohydrindene, $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}\cdot\text{NOH}$, by means of stannous chloride (*Trans.*, 1911, xcix., 1306), could not be obtained pure, owing to the ease with which it is oxidised by the oxygen of the air. It was characterised, however, by the condensation products which it yields with aromatic aldehydes. These substances, which may be represented by the general formula—



are not very stable, and are readily hydrolysed to the compounds from which they are formed. The blue coloration which is produced on exposure of diketohydrindamine to moist air is due to the formation of the analogue of

murexide, which is the ammonium salt of diketohydrindylidenediketohydrindamine—



This can be prepared from hydrindantin under conditions similar to those which served for the production of murexide from alloxantin (Piloty and Finckh, *Annalen*, 1904, cccxxxiii., 27). The ketone—



corresponding with this salt was also isolated; it is, however, readily decomposed by mineral acids.

By the action of triketohydrindene hydrate on uramil dissolved in potassium hydroxide, the potassium salt of diketohydrindylideneuramil—



is produced; it dissolves in water to yield reddish violet solutions, which are decolorised by dilute hydrochloric acid.

It was found that the colour-reaction which the triketone gives with amino-acids is based on the formation of the ammonium salt of diketohydrindylidenediketohydrindamine.

205. "The Constitution of the Organic Ferrocyanides." By ERNALD GEORGE JUSTINIAN HARTLEY. (*Trans.*, 1911, 1549).

In order to throw some light on the constitution of the ferrocyanides, the decomposition of tetramethyl ferrocyanide, $(\text{CH}_3)_4\text{FeC}_6\text{N}_6$, and hexamethyl ferrocyanogen dihydrogen sulphate, $(\text{CH}_3)_6\text{FeC}_6\text{N}_6\text{H}_2(\text{SO}_4)_2$ (*Trans.*, 1910, xcvi., 1066, 1725), has been studied. The former, on heating with concentrated sulphuric acid, gave a mixture of ammonium and methylammonium sulphates, whilst the latter, under similar conditions, gave only methylammonium sulphate. Decomposition of the hexamethyl compound with sodium hydroxide also led only to the formation of methylamine derivatives. From this the conclusion is drawn that all the methyl groups are attached directly to nitrogen atoms in both the substances examined.

206. "Contributions to the Chemistry of the Terpenes. Part IX. The Oxidation of Camphene with Hydrogen Peroxide." By GEORGE GERALD HENDERSON and MAGGIE MILLEN JEFFS SUTHERLAND. (*Trans.*, 1911, 1539).

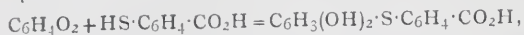
Camphene, when dissolved in glacial acetic acid, is oxidised by a 30 per cent aqueous solution of hydrogen peroxide, yielding a mixture of products, which includes both acids and neutral compounds. The acid present in largest quantity, camphylic acid, $\text{C}_9\text{H}_{15}\cdot\text{CO}_2\text{H}$, is a crystalline solid, m. p. 95° , and when heated with acetic anhydride is transformed into the isomeric isocamphenilanic acid. From the chloride of camphylic acid, $\text{C}_9\text{H}_{15}\cdot\text{COCl}$, by bromination and subsequent treatment of the product with water, bromocamphylic acid, $\text{C}_9\text{H}_{14}\text{Br}\cdot\text{CO}_2\text{H}$, was obtained in crystals, melting at 210° . When heated with aqueous sodium carbonate the bromo-acid is converted into the crystalline hydroxycamphylic acid, $\text{C}_9\text{H}_{14}(\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 245° . The latter does not give a ketone when oxidised with lead peroxide.

Camphenilone, $\text{C}_9\text{H}_{14}\text{O}$, a ketone which has been prepared from camphene in other ways, is the chief component of the mixture of neutral oxidation products. isocamphenilanaldehyde, $\text{C}_9\text{H}_{15}\cdot\text{CHO}$, which is also present, is very similar in properties to the isomeric camphenilanaldehyde, but yields isocamphenilanic acid on exposure to the air. Its semicarbazone melts at 191 — 192° , and the semicarbazone prepared from camphenilanaldehyde appears in reality to be this compound. Among the other neutral products, together with a very little camphene glycol, $\text{C}_{10}\text{H}_{16}(\text{OH})_2$, and a trace of a crystalline substance which melts at about 69° , there occurs a compound which

apparently has the formula $C_6H_{16}O_2$. When heated to a high temperature with phthalic anhydride this compound yields a crystalline ester, from which, by hydrolysis, an alcohol of the formula $C_6H_{16}O$ is obtained.

207. "Synthesis of Derivatives of Thioxanthone. Part III. 1:4-Dihydroxythioxanthone." By HANS THACHER CLARKE and SAMUEL SMILES. (*Trans.*, 1911, 1535).

When *p*-benzoquinone is allowed to react with *o*-thiolbenzoic acid, 2'-carboxy-2:5-dihydroxydiphenyl sulphide is produced:—



The latter on treatment with cold sulphuric acid loses water, and is converted into 1:4-dihydroxythioxanthone. $C_6H_4 < \begin{smallmatrix} CO \\ S \end{smallmatrix} > C_6H_2(OH)_2$.

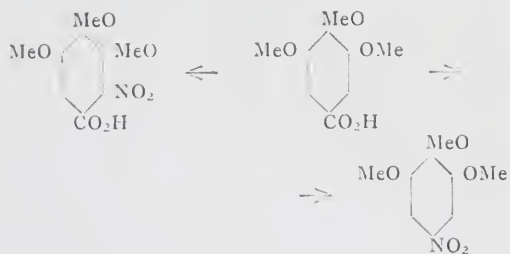
This substance and its salts are strongly coloured, but do not appear to be of practical value as dye-stuffs.

208. "Optically Active Derivatives of 1-Methylcyclohexylidene-4-acetic Acid." By WILLIAM HENRY PERKIN, jun., and WILLIAM JACKSON POPE. (*Trans.*, 1911, 1510).

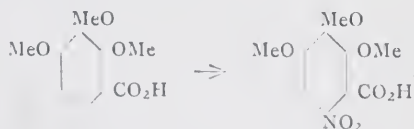
The optical activity of *d*- and *l*-1-methylcyclohexylidene-4-acetic acid is due to the configuration of the molecule exhibiting a particular type of enantiomorphism unassociated with asymmetry of any particular atom present; the authors give the name "centrosymmetric" to this type of enantiomorphism. They now describe the conversion of optically active centrosymmetric compounds into substances containing an asymmetric carbon atom, and also the reverse change; they show that the optical activity of the original substance is preserved during the change in either direction. The change from the one to the other type of enantiomorphous configuration is thus unaccompanied by optical inversion.

209. "Substitution in Aromatic Hydroxy-compounds. Part I. The Action of Nitric Acid on Gallic Acid Trimethyl Ether and Pyrogallolcarboxylic Acid Trimethyl Ether." By VICTOR JOHN HARDING. (*Trans.*, 1911, 1585).

Gallic acid trimethyl ether on treatment with nitric acid under varying conditions undergoes the following reaction:



Pyrogallolcarboxylic acid trimethyl ether under similar conditions yields only the nitro-acid:—



No substitution of the carboxyl group was observed. As the substitution of carboxyl groups by the nitro-group is partly dependent on its position in the molecule, the hypothesis is put forward that carboxyl-substitution is governed by those forces in the molecule which direct substitution in the parent phenol ether, and that there is no real difference between hydrogen-substitution and carboxyl-substitution.

210. "The Solubility of Cuprous Oxide in Aqueous Ammonia Solutions, and the Composition of the Cuprous-ammonia Complex." By FREDERICK GEORGE DONNAN and JOHN SMEATH THOMAS. (*Trans.*, 1911, 1788).

The solubility of crystalline cuprous oxide in solutions of ammonia of different concentrations has been determined at 25°. It is found that for a certain range of ammonia concentrations the concentration of total copper is approximately proportional to the square root of the "free" ammonia. From this result the conclusion is drawn that in these solutions the cuprous-ammonia hydroxide present is mainly of the type $(Cu \cdot NH_3)OH$.

211. "The Acid Character of Gallotannic Acid." By RAMNI PANIKER and EDMUND STIASNY. (*Trans.*, 1911, 1819).

The authors have applied Bredig and Fraenkel's method to the determination of the hydron concentration of gallotannic acid. This method is based on the dissociation of diazoacetic ester by the catalytical action of hydriions, the concentration of which determines the speed of the development of nitrogen. Different samples of gallotannic acid, prepared by different and partly new—methods of purification, were used, and their acid character was found distinctly greater than could be explained by the presence of phenolic groups only, thus leading to the conclusion that free carboxylic groups are present. This confirms the views of Schiff and Nierenstein, but does not agree with those of Böttiger (*Ber.*, 1884, xvii., 1503, Walden (*Ber.*, 1898, xxxi., 3170), and Dekker (*Ber.*, 1906, xxxix., 2497). The authors are of the opinion that even the purest gallotannic acid obtainable is no single substance, but a mixture of at least two components of allied character.

212. "Synthesis of Polypeptides of α -Amino-*n*-nonoic Acid with Glycine, Alanine, Valine, Leucine, Asparagine, and Aspartic Acid." By ARTHUR HOPWOOD and CHARLES WEIZMANN. (*Trans.*, 1911, 1577).

As polypeptides of α -amino-*n*-nonoic acid with glycine and other amino-acids probably occur in the degradation products of the proteins contained in beetroot, the leaves of *Polygonum roseum*, and other plants, the authors have prepared the following derivatives of α -amino-*n*-nonoic acid: α -Bromo-*n*-nonoyl chloride, $C_8H_{16}Br \cdot COCl$, prepared by heating α -bromo-*n*-nonoic acid with phosphorus pentachloride, is a colourless liquid boiling at 108–110°/9 mm. When condensed with glycine in the presence of sodium hydroxide it gives α -bromo-*n*-nonoylglycine, $C_8H_{16}Br \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, which forms a mixture of colourless rhombic plates and rhombic prisms, melting at 115.5–117°. The crystals are only sparingly soluble in cold water or benzene, but readily so in alcohol, ether, or alkalis.

α -Amino-*n*-nonoylglycine,—



is prepared by heating α -bromo-*n*-nonoylglycine with concentrated aqueous ammonia. It forms a mixture of colourless monoclinic needles and rhombic plates, which sinters at 205°, and melts and decomposes at 215–216°. It is fairly soluble in water, almost insoluble in alcohol or benzene, but readily soluble in alkalis or mineral acids. Like the proteins, it yields a white amorphous precipitate with phosphotungstic acid, but unlike the corresponding dipeptide, α -aminolaurylglycine, it is not hydrolysed by enzymes or bacteria.

Somewhat similar bromo compounds are prepared by the condensation of α -bromo-*n*-nonoyl chloride with alanine, valine, leucine, asparagine, and aspartic acid, and these on heating with ammonia yield the corresponding dipeptides. Similarly, the tripeptide *leucyl*- α -amino-*n*-nonoylglycine is prepared by condensing α -amino-*n*-nonoylglycine with α -bromohexoyl bromide, and then displacing the bromine by the amino-group through the action of ammonia.

213. "Latent Heats of Vaporisation of Mixed Liquids." (Part I.). By DAN TYRER. (*Trans.*, 1911, 1633).

In order to determine the latent heats of mixed liquids the liquid is contained in a bottle provided with a thermometer ground into its neck. In the liquid is immersed a coil of platinum wire of known resistance, through which is passed a known current. The liquid, which has first been heated to its boiling-point by an external bath, immediately boils, and the amount of liquid evaporated by the known amount of electricity is determined by weighing before and after. This gives all the necessary data. As, however, with mixed liquids the boiling-point rises as the evaporation proceeds, a correction must be made for heat used in raising the temperature of the liquid. This is determined in a second experiment by determining the heat capacity of the liquid with the containing vessel.

Measurements have been made for three cases of normal mixtures. The latent heat cannot be regarded as a linear function of the composition of the mixture, but depends also on the composition of the vapour.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, October 27th, 1911.

Prof. H. L. CALLENDAR, F.R.S., President, in the Chair.

A PAPER ON "Further Observations on the Afterglow of Electric Discharge and Kindred Phenomena," was read by the Hon. R. J. STRUTT, F.R.S.

It is shown that ozone prepared by means of the Siemens ozone tube used at atmospheric pressure is able, when mixed with nitric oxide, to give the greenish yellow afterglow flame. This result is only attained, however, when the ozone has been concentrated by fractional distillation. A blue glow is obtained under the same conditions with sulphuretted hydrogen and ozone.

The effect of sulphur compounds in improving the air glow noticed by the older experimenters is shown to be due not to any direct intervention of these bodies in the reaction, but to their power of destroying organic matter prejudicial to ozone. When once this is got rid of, the sulphur compounds are of no further advantage.

It is found that pure oxygen does not give an afterglow. The afterglow seen in electrodeless bulbs containing oxygen is due to some interaction with water vapour.

The luminosity given out when ordinary spring water is shaken with ozone is shown to be due to oxidation of peaty matter contained in it. Brown peat water gives greatly enhanced luminosity.

DISCUSSION.

Mr. A. CAMPBELL inquired whether quartz would not be better than glass in vacuum tube work for preventing occlusion of moisture and gases.

Mr. EGERTON asked whether the afterglow might not be due to ozone decomposing into oxygen. In this case both liquid air and phosphoric pentoxide would prevent the glow by removing the ozone.

The AUTHOR replied that quartz would undoubtedly be superior to glass, but pointed out the difficulties of working with it, and the impossibility of making sealed joints. In reply to Mr. Egerton he stated that there was some evidence that moisture was necessary for the afterglow in oxygen, as it was found that the afterglow disappeared at the same time as the red hydrogen line.

A paper on "Homogeneous Fluorescent X-Radiation of a Second Series," by Prof. C. G. BARKLA and J. NICOL, was read by Prof. BARKLA.

It was shown by one of the writers that the fluorescent X-radiations emitted by elements exposed to primary Röntgen radiation can be arranged in series, one radiation in a particular series being emitted by each element, and the radiation belonging to that series becoming more pene-

trating with an increase in the atomic weight of the radiating element (*Proc. Camb. Phil. Soc.*, May, 1909). The homogeneity of radiations of only one series (the K series) was shown by Barkla and Sadler. This paper describes experiments showing the homogeneity of fluorescent X-radiations in the second series (the L series), and exhibiting the homogeneity of radiations of the two series from a number of elements. Details are given of the observations on the radiations from barium. Similar results are recorded in the case of the radiations from iodine, antimony, and silver.

The homogeneous fluorescent radiations of different series are emitted simultaneously by an element exposed to Röntgen radiation of more penetrating type than either. The fluorescent X-radiations can thus be analysed into well defined radiations widely different in penetrating power, and may be said to give a line spectrum in X-rays.

The absorptibility of the fluorescent radiations is given by the following values of λ/ρ , where λ is the coefficient of absorption of these radiations in aluminium of density ρ .

Ag radiator : (Series K) [2.5] ; (Series L) 700	
Sb " " 1.21 " 435	
I " " 0.92 " 300	
Ba " " 0.8 " 224	

DISCUSSION.

Dr. S. RUSS inquired as to the mechanism of the production of scattered radiations, and asked whether scattered radiation would be produced by homogeneous radiations.

Prof. C. G. BARKLA, in reply, said that scattered radiation was produced by a pulse passing over an electron disturbing it, and so causing it to radiate a pulse of the same wave-length or hardness. No satisfactory explanation of either X-ray fluorescence or ordinary fluorescence had been given, but he pointed out that after the pulse had passed over an electron the latter would continue to vibrate with its natural frequency.

NOTICES OF BOOKS.

A Treatise on Chemistry. By the Right Hon. Sir HENRY E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Vol. I. "The Non-metallic Elements." New Edition. London: Macmillan and Co., Ltd. 1911. (21s. net).

THERE is no better treatise on descriptive chemistry extant than Roscoe and Schorlemmer's standard work, and a new edition of it, edited by Sir Henry Roscoe and Dr. J. C. Cain, will be welcomed enthusiastically. In it the well known excellent features which have led to its wide adoption in colleges and schools—the clear illustrations, the interesting historical summaries, and the descriptions of technical processes—are still prominent, and the latest discoveries and applications are included, with discussions of all the most recent experimental work.

Chemistry. An Elementary Text-book. By WILLIAM CONGER MORGAN, Ph.D., and JAMES A. LYMAN, Ph.D. New York: The Macmillan Co. 1911.

THE authors of this book have a great belief in the importance of making chemistry appear to be a subject of human as well as scientific interest to the student, and have lost no opportunity of emphasising the nature and value of its applications in every day life. They give a great many good illustrations to impress upon the mind the countless natural phenomena which are manifestations of chemical reactions, and the continual uses which are made of the facts which chemical research has accumulated. All this is excellent, and should make the beginnings of the science vivid and attractive. But the spade-work of learning a new subject has to be done, and the authors have possibly not entirely succeeded in hitting

upon the best method of giving their readers an opportunity of obtaining a mastery of the facts and principles of the science. The laws of chemistry are introduced too early in the book, and it is wiser generally speaking to defer equations till the atomic theory has at any rate been briefly explained. There is, moreover, too much detail in the early parts of the book. On the other hand, the summaries of each chapter will be found useful, and the questions are certainly novel and stimulating and of a type rather unusual in a scientific text-book.

The Electrical Nature of Matter and Radio-activity. By HARRY C. JONES. Second Edition. London: Constable and Co., Ltd. 1911. (8s. net).

THIS book is probably well known to many of the readers of the CHEMICAL NEWS as giving an accurate and well balanced account of investigations of radio-activity and the explanatory theories which have been put forward. The new edition has been thoroughly revised, and a good deal of fresh matter has been introduced into it. This includes recent researches on the mass of the α -particle, the production of β -particles, and the action of the α -particles on photographic and fluorescent plates. Fresh work on induced activity is also discussed.

Das Kristallisationsmikroskop und die Damit Gemachten Entdeckungen Insbesondere die der Flüssigen Kristalle. ("The Crystallisation Microscope and the Discoveries made with it, especially that of Liquid Crystals"). By O. LEHMANN. Braunschweig: Friedrich Vieweg und Sohn. 1910.

NO better subject could have been chosen for discussion in a volume, which has been issued in commemoration of the birthday of the Grand Duke Friedrich II. of Baden, than the crystallisation microscope, and Dr. Lehmann has much that is interesting and of vital importance to say on the subject, and can write on it with more authority than any man living. He first describes the discovery of the microscope and the structure of the earlier instruments, and in later chapters gives details and illustrations of its latest refinements. The discoveries made with it are discussed in full one by one, first that of the temperature of transition, then plastic crystals, anomalous mixed crystals, liquid crystals, and finally apparently living crystals. When it is realised that the use of one instrument has led to this extraordinary series of investigations even the immediate results of which are hardly yet known, it will at once be admitted that no opportunity should be lost of spreading the knowledge of it as widely as possible.

CORRESPONDENCE.

REFORM OF CHEMICAL AND PHYSICAL CALCULATIONS AND PROF. F. W. CLARKE'S EIGHTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS.

To the Editor of the *Chemical News*.

SIR,—Prof. F. W. Clarke's report published in CHEMICAL NEWS, vol. civ., p. 5 *et seq.*, is very interesting, and the data given deserve closer examination.

Hydrogen. The atomic weight is re-calculated by Grinnell Jones "from all trustworthy determinations," and finally determined $H = 1.00775$, and by Prof. Clarke re-calculated and found $H = 1.00779$, which is *very near* to Prof. Hinrichs' determination, $H = 1.00781$, published in CHEMICAL NEWS, vol. xcix., p. 229; but Prof. Clarke has omitted to state that the decimal fraction 0.00779 in his determination (or 0.00781 as found by Hinrichs) is the

weight of the pantogene (π), which fills the empty space between the atoms of hydrogen and all other empty spaces in the Universe. The atomic weight of *pure* H is = 1.0000, but in nature we always find H united with π as $1H + 0.00781\pi$, and as *proved* in my article in CHEMICAL NEWS, vol. xcix., p. 229, the atomic weight of *pure* H, C, N, and O is = 1 : 12 : 14 : 16 *exactly* without any decimals. Besides these four gases, the German Atomic Weight Table of 1909 and Prof. Hinrichs' tables show now twenty other elements in whole figures without decimals, and if these and their combinations are adopted as basis for finding and calculating the true atomic weight of other elements we may hope to get out of the present atomic confusion, and get a table of atomic weights in which we can recognise the harmonic simplicity which rules everywhere in God's Creation.

O = 16 is, of all the substances mentioned in Prof. Clarke's report, the only one with atomic weight in round numbers, and similar ones only can be found if these are used to calculate the atomic weights of other elements, and the confusion will be increased; but if we use the substances whose plain atomic weights have been ascertained, and simplify the method of calculation, we may get a good result.

A few examples from Prof. Clarke's report may explain my scheme. In CHEMICAL NEWS, vol. civ., p. 5, we find:—

Nitrogen.—Atomic weight $N = 14.0101$, $O = 16$, and the weight of $2O_2$ combining with N_2 , and the weight of the resulting N_2O_4 ; repeating the calculation with $N = 14$: $O = 16$, then $64O$ combining with $28N$ gives the ratio $7/16$, and—

$0.6160O \times 7/16$	unite with	$0.2605 N$	to form	$0.8855 N_2O_4$
$1.2860O \times 7/16$	"	$0.5626 N$	"	$1.8486 N_2O_4$
$1.4801O \times 7/16$	"	$0.6475 N$	"	$2.1276 N_2O_4$

Silver and Iodine.—Clarke's atomic weight, $Ag = 107.864$, $I = 126.913$; Hinrichs' atomic weight, $Ag = 108$, $I = 127$. Clarke's *ratio* mean, 0.849906; Hinrichs' *ratio*, $108/127 (= 0.85049)$.

The differences in the results are small, but the convenience of an atomic weight table, $H = 1$: $O = 16$ and all elements in round numbers, would be enormous. The author of "Reform of Chemical and Physical Calculations" (published 1897) who writes these lines is now over ninety years old, but hopes that others will take up the work and complete it.—I am, &c.,

C. J. T. HANSSEN, C.E.

Copenhagen, Valdemarsgade 3,
October 30, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 12, September 18, 1911.

Lactarinic Acid, obtained from Mushrooms.—J. Bougault and C. Charaux.—Lactarinic acid exists in the free state in certain varieties of mushrooms, and can readily be extracted by treatment with alcohol at 90° . The acid fuses at 87° . It is insoluble in water, but dissolves in most organic solvents on warming. Ether and chloroform are the best solvents. Its alkaline salts are only very slightly soluble in cold water, but dissolve on heating. The formula of the acid is $C_{18}H_{34}O_3$, and it is a keto-stearic acid.

Nos. 13 and 14, September 25 and October 2, 1911.
These numbers contain no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xliii., No. 13, 1911.

Preparation of Pure Aromatic Telluronium Compounds.—Charles Lederer.—To prepare triphenyl telluronium compounds, magnesium ribbon is dissolved in benzene bromide, and the solution is added to a solution of tellurium tetrachloride in ether. The whole is then cooled, and the liquid constituents are separated from the solid, well washed with ether, and extracted with alcohol. The solid products consists of triphenyl-telluronium bromide, the corresponding chloride, magnesium salt, and diphenyl-telluronium iodide. The alcoholic residue is dissolved in water, and decomposed with potassium iodide, when the telluronium iodide separates. The residue insoluble in water is re-crystallised from chloroform. It consists of diphenyl-telluronium diiodide. From the residue remaining after extraction with alcohol, diphenyl-telluronium dibromide can be separated by means of chloroform. The tri-*p*-tolyl compounds can be obtained similarly.

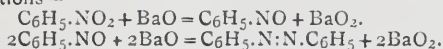
Iodine : Tin Ester Compounds.—Bruno Emmert and Wilhelm Eller.—When tin and iodo-acetic ester are warmed together di-iodo-tin-diacetic ester, $I_2Sn(CH_2.CO_2C_2H_5)_2$, is obtained. A small quantity of iodine is necessary to start the reaction. Although the product thus obtained structurally corresponds to the dialkyl tin iodides it differs from these substances in some important reactions. Thus no oxide of the ester compound can be prepared. When magnesium alkyl bromide acts on these esters a good yield of tin tetraphenyl is obtained:—



Tin tetraethyl can be prepared similarly, substituting magnesium ethyl iodide for magnesium phenyl bromide.

Iron and Magnesium Arsenides.—Siegfried Hilpert and Theodor Dieckmann.—Chemically pure arsenides are obtained when arsenic vapour acts upon a metal under pressure and at a high temperature. Thus, if finely powdered iron is heated to 700° with excess of arsenic in a Jena glass tube for six to eight hours, the compound $FeAs_2$ is produced as a silver-grey powder of sp. gr. 7.38. By distilling off the arsenic in a current of hydrogen at 680° $FeAs$ is obtained. The pure manganese arsenide, $MnAs$, can be prepared by the same method. It is noteworthy that while the two iron arsenides, $FeAs$ and $FeAs_2$, are quite non-magnetic, $MnAs$ is ferromagnetic. Metallic phosphides can be prepared by an analogous method.

Barium Oxide as a Reducing Agent.—Th. Zerevitinoff and Iw. Ostromisslensky.—When a mixture of nitrobenzene and barium oxide is heated to 208° nitrosobenzene is formed. If nitrobenzene vapour is led over heated barium oxide the reduction proceeds further, the chief product being azobenzene; some phenazine and aniline and a very little ammonia are also formed. Barium oxide reduces *p*-nitrotoluene to *p*-toluidine and azo-toluene. *o*-Nitrotoluene gives only *o*-toluidine. The reactions with nitrobenzene are represented by the equations—



To explain the formation of aniline and ammonia it must be supposed that the nitrobenzene undergoes oxidation during the reaction.

Tantalum, Tungsten, and Hydrogen.—A. Sieverts and E. Bergner.—The authors have determined the solubility of hydrogen in tantalum up to 1330°; if the pressure of the gas is constant the solubility decreases as the temperature is raised, and at a given temperature it is proportional to the square root of the gas pressure. When tantalum wire is heated to redness in hydrogen it undergoes a change of structure, which persists when the hydrogen is extracted by ignition *in vacuo*. Nitrogen

reacts slowly with tantalum at 900°, forming a nitride. At 1500° tungsten dissolves only a very small quantity of hydrogen. Nitrogen does not react with tungsten at 1500°.

Constituent of Coal.—Amé Pictet and Louis Ramseyer.—The authors have employed two methods to obtain definite compounds from coal; firstly, extraction with organic solvents, and, secondly, distillation under diminished pressure at as low a temperature as possible. They have thus isolated a hexahydride of fluorene. At a higher temperature it loses hydrogen and yields fluorene. This transformation is one source of the formation of the aromatic hydrocarbons of tar as well as of the hydrogen of coal-gas. The authors' experiments to a certain extent confirm Donath's hypothesis, that coal was a mixture of originally liquid compounds, which have gradually become solid owing to polymerisation.

Vanadium Bromides.—Otto Ruff and Herbert Lickfett.—When bromine or a mixture of bromine and sulphur bromide acts at a red heat on a mixture of vanadium pentoxide and sulphur, a product is obtained which, when heated to 240° *in vacuo*, gives pure vanadium oxydibromide, $VOBr_2$, as a residue, sulphur bromide and bromine distilling off. If the temperature of the residue is raised to 360° the vanadium oxydibromide sublimes and partially decomposes, leaving as residue a violet product, vanadium oxybromide, $VOBr$, which has not been prepared before. When heated *in vacuo* to 480° vanadium tribromide sublimes, and the trioxide remains behind.

Vanadium Fluorides.—Otto Ruff and Herbert Lickfett.—When fluorine acts on vanadium or the anhydrous halogen salts it is difficult to separate the mixture of fluorides formed, but compounds of tri-, tetra-, and pentavalent vanadium can readily be obtained by the action of anhydrous hydrofluoric acid on the vanadium haloids. Thus from pure vanadium trichloride the trifluoride, VF_3 , is obtained, from the tetrachloride VF_4 , from the oxydibromide VOF_2 , and from the oxytrichloride VOF_3 . When vanadium tetrafluoride is heated above 300° gas is evolved, the tetrafluoride decomposing quantitatively into the trifluoride, and the gaseous pentafluoride VF_5 . Thus vanadium tetrafluoride can be prepared most easily by heating the tetrafluoride to redness in a current of nitrogen.

Action of Calcium Fluoride on Vanadium Pentoxide.—Wilhelm Prandtl and Hermann Manz.—When a mixture of V_2O_5 and CaF_2 is heated in an open crucible, some of the vanadium volatilises. The loss of V_2O_5 is from 12 to 15 per cent of the amount originally present in the mixture $CaF_2 + V_2O_5$, and 30 per cent in the mixture $V_2O_5 + 5CaF_2$. Apparently the sublimation of V_2O_5 depends on the intermediate formation of a volatile fluoride or oxyfluoride, which is then decomposed into V_2O_5 and HF.

Tetra-alkyl Silicanes.—Artur Bigden.—By the action of alkyl magnesium bromide on silicon tetrachloride the author has prepared various derivatives of silicane. SiH_4 . These include $(CH_3)_4Si$, $(CH_3)_3SiC_2H_5$, $(CH_3)_3Si(n-C_3H_7)$, $(CH_3)_3Si(C_2H_5)_2$, $(CH_3)_3Si(n-C_4H_9)$, $(CH_3)_2Si(C_2H_5)(n-C_3H_7)$, $(CH_3)_2Si(i-C_3H_7)_2$, $(CH_3)_2Si(C_2H_5)(i-C_3H_7)$, $(C_2H_5)_3Si$. All these compounds are volatile liquids smelling like petroleum. They are very stable, being unaffected by concentrated sulphuric acid or by alkalis. At a high temperature they are oxidised by concentrated nitric acid. Chlorine replaces the hydrogen in them in the cold, and bromine on warming. They are all inflammable, burning with a luminous flame, and yielding silicon dioxide. When they are mixed in a state of vapour with air or oxygen and heated they explode.

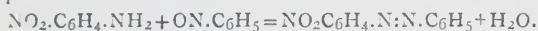
Ferromagnetic Compounds of Manganese.—E. Wedekind and Th. Veit. Manganese bismuthide, $MnBi$, is fairly strongly ferromagnetic. The selenide and telluride are both feebly magnetic. The silicide, Mn_2Si , shows no magnetic properties, and the sulphide, MnS , is feebly magnetic, and becomes decidedly more so when it is heated. The carbide, Mn_3C , is magnetic.

Atti della Reale Accademia dei Lincei.
Vol. xx., (II.), No. 3, 1911.

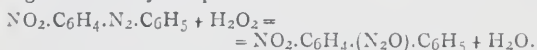
Derivatives of Oxyhydroquinone.—E. Bargellini and S. Aureli.—By the action of potassium or ammonium persulphate on the 4-methyl ether of 2,4-dioxyacetophenone, a compound of formula $C_9H_{10}O_4$ is obtained. This is the monomethyl ether of trioxyacetophenone. On etherification with dimethyl sulphate it yields the trimethyl ether of 2,4,5-trioxyacetophenone together with a dimethyl ether, $C_{10}H_{12}O_4$. This synthesis throws light upon the constitution of the original dioxyacetophenone.

No. 4.

Researches on Azoxy-compounds.—A. Angeli and Luigi Alessandri.—The authors prepared the nitroazobenzene necessary for their experiments by the action of *p*-nitroaniline on nitrosobenzene:—



With concentrated nitric acid nitroazobenzene gives a red powder, which is *p*-*p*-dinitroazobenzene:—
 $NO_2.C_6H_4.N:N.C_6H_4.NO_2$. When oxidised with H_2O_2 it gives an azoxy-compound:—



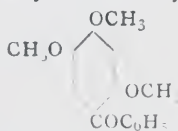
When nitric acid acts on this azoxy-compound the product is *p*-*p*-dinitroazoxybenzene, which appears to differ from the compound formed when nitric acid acts on azoxybenzene in the position of its oxygen atom, thus:—
 $C_6H_5.N = N.C_6H_4.NO_2$ and $C_6H_5.N = N.C_6H_4.NO_2$



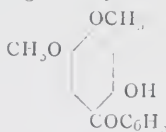
and



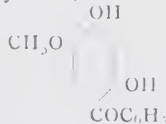
Derivatives of Oxyhydroquinone.—G. Bargellini and Ermanno Martegiani.—When the chloride of benzoic acid condenses with the trimethyl ether of oxyhydroquinone in presence of sublimed aluminium chloride, the products are:—1. The trimethyl ether of trioxybenzophenone,—



2. The corresponding dimethyl ether,—



3. The monomethyl ether,—



Similar condensations can be effected with the chlorides of anisic and phenylacetic acids.

Influence of Auxochromes on Phototropism.—M. Padoa and L. Santi.—To determine the influence of auxochrome groups on the character and intensity of phototropism, the authors have studied the products obtained by the action of anisidrazine on various aldehydes. The results are as follows:—*Phototropic compounds*, anisidrazones of benzaldehyde, cinnamic aldehyde, cuminal, piperonal, vanillin. *Nonphototropic compounds*, anisidrazones of anisaldehyde, *p*-toluic aldehyde, salicylic aldehyde.

Researches on Strychnine and Brucine.—R. Ciusa and G. Scagliarini.—By the action of bromine on strychnine dissolved in glacial acetic acid a dibromide, $C_{21}H_{22}O_2N_2Br_2$, is obtained. It readily gives up a molecule of hydrobromic

acid, giving a monobromide which fuses at 222–223°. The same monobromide is obtained by Lobisch and Schoop's method; *i.e.*, the action of bromine on a sulphuric solution of strychnine. Bromine acts on brucine to give a perbromide, $C_{23}H_{26}O_4N_2Br_5.H_2O$. The action of potassium chlorate on a hydrochloric acid solution of strychnine in the cold gives a tetrachlorostychnine. On warming an octochlorostychnine is obtained.

MISCELLANEOUS.

Royal Institution.—The Eighty-sixth Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Dr. P. Chalmers Mitchell, D.Sc., LL.D., F.R.S., Secretary of the Zoological Society, his subject being "The Childhood of Animals." The Lectures will be delivered on the following dates at 3 o'clock:—Thursday, December 28, December 30, 1911, January 2, 4, 6, and 9, 1912.

Royal Institution. A General Monthly Meeting of the members of the Royal Institution was held on the 6th inst.; the Duke of Northumberland, K.G., President, in the Chair. Miss C. A. Clarendon, Lord Congleton, and Mr. A. Hall were elected Members. The Chairman reported the decease of the Right Hon. Earl Cathcart, D.L., J.P., a Manager, Prof. G. L. Van der Mensbrugghe, Prof. W. V. Spring, and Prof. L. J. Troost, Honorary Members of the Royal Institution, and resolutions of condolence with the families were passed.

Royal Society of Arts.—The Royal Society of Arts begins its 158th Session on Wednesday, November 15th, with an Address from Lord Sanderson, G.C.B., the Chairman of the Council. Five meetings are announced before Christmas, at which papers will be read on "The Industrial Progress of America," by Prof. James Douglas, LL.D.; on "The Efficiency of the Aeroplane," by A. E. Berriman; on "British Guiana," by J. A. J. de Villiers; on "London Transport," by W. Yorath Lewis; and on "Bengal Fisheries," by Dr. J. Travers Jenkins. Four Cantor Lectures on "The Carbonisation of Coal" will be delivered by Prof. Vivian Lewes, and two Juvenile Lectures on "Soap Bubbles" will be given in January by C. V. Boys, F.R.S. A long list of papers for the meetings to be held after Christmas is also published.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Microscopical, 8. "A Geometric Slide Photomicrographic Apparatus," by J. E. Barnard. "British Enchytraeids—II., The Genus *Fritteria*," by Rev. H. Friend. Exhibition of Slides of Rock Sections presented by Mr. H. J. Grayson.

Royal Society of Arts, 8. Opening Address of the 158th Session, by Lord Sanderson, G.C.B., K.C.M.G., &c.

THURSDAY, 16th.—Royal Society, 8. "The Influence of Ionised Air on Bacteria," by W. M. Thornton. "Permeability of the Yeast Cell," by S. G. Paine. "The Intrinsic Factors in the Act of Progression in the Mammal," by Dr. T. G. Brown. "Ventilation of the Lung during Chloroform Narcosis," by G. A. Buckmaster and J. A. Gardner. "Refractive Indices of the Eye Media of some Australian Animals," by Dr. J. L. Jona.

Chemical, 8.30. "Influence of Neutral Solvents on Velocity of Reaction—Part I., Transformation of Anisylaldehyde in various Solvents," by T. S. Patterson and H. H. Montgomery. "Organic Derivatives of Antimony—Part II., The Orienting Influence of Antimonic Substituents in the Benzene Nucleus," by G. T. Morgan and Miss F. M. G. Micklethwait. "Chemical Examination of Calabar Beans," by A. H. Salway. "Copper Salts and their Behaviour with Alkalis," by S. U. Pickering. "Contributions to the Chemistry of the Terpenes—Part XII., Synthesis of a Mentha-diene from Thymol, and of a Dihydrodiethyl Benzene from Phenol," by G. G. Henderson and R. Boyd.

THE CHEMICAL NEWS.

VOL. CIV., No. 2712.

RECENT DEVELOPMENTS OF THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

By A. E. JOHNSON, B.Sc (Lond.), F.I.C.

WHILE reading with great interest the papers on the above subject by Chamot, Pratt, and Redfield, published in the CHEMICAL NEWS (vol. civ., p. 146 *et seq.*), I was considerably surprised to read the following (in reference to the various kinds of reagents that have from time to time been proposed):—

- C. Those made by mixing phenol and concentrated sulphuric acid and adding thereto a little concentrated hydrochloric acid (Johnson, CHEMICAL NEWS, 1890, lxi., 15, &c.).
- D. Those made by heating a mixture of phenol and concentrated sulphuric acid (Gill, &c.).

This indicates clearly enough that, according to the authors, I advocated simply *mixing* the reagents, whereas, as a matter of fact, the main object of my communication on that occasion was to draw attention to the primary importance, when making this reagent, not only of heating the mixture of phenol and sulphuric acid, but of heating it for a sufficient length of time. I had found some time previous to 1890 that even four hours' digestion was insufficient, and that to get a really satisfactory reagent—that is, one that could be depended upon to give a pure yellow colour with nitrates—about eight hours' digestion was necessary. I have met with several chemists who have been troubled with a phenolsulphonic acid solution that gave a bright green colour with nitrates, and, I may add, I once (previous to 1890) made one myself. The paper under discussion gives abundant evidence of the fact that this is quite a common experience, and the principal reason why treatment of the nitrate residue in the cold has been advocated appears to be that the reagent used would not stand moderate heating with a nitrate without developing a more or less pronounced green tinge. The reagent produced when my directions for making it are carefully followed will be found to give a more or less deep red colour, according to the amount of nitrate present, when the beaker is allowed to stand on the top of the water-oven for fifteen minutes; it never develops a green colour. Before fixing on the period of eight hours, I used at one time to withdraw, by means of a long graduated 5 cc. pipette, 1 cc. of the hot liquid, dilute it with 1½ cc. of water, and add ½ cc. HCl, mix, and add 1 cc. of the reagent so obtained to a dry residue from 1 cc. of the strong standard KNO₃ solution in a small beaker on the water-oven. After fifteen minutes' standing this was then diluted, ammonia (or potash) added in excess, and the colour of the solution, diluted to 100 cc. in a Nessler glass, observed. If a green tinge was produced, the digestion was continued for another hour, when another similar test was made. In this way I found that eight hours' digestion was always more than sufficient. Moreover, by this prolonged digestion a newly made solution will give the same results as one that has been made for several months. I should like to add that 1 cc. of my reagent suffices to determine nitric nitrogen up to about 1.5 parts per 100,000. Above that amount 5 cc. or less of the water under examination should be taken for the determination.

The authors direct that their reagent be made with "fuming sulphuric acid (13 per cent SO₃). I have not been able to find a source of an acid of this composition. Kahlbaum supplies fuming sulphuric acid containing

"about 7, 20, 33, 50, 70, and 80 per cent SO₃." Hence I take it that 50 cc. of fuming sulphuric acid (20 per cent SO₃) and 175 cc. of pure sulphuric acid, together with 25 grms. of pure phenol, might be used for making the reagent recommended, in place of the quantities given by the authors. This reagent requires to be brought into intimate contact with the nitrate residue by rubbing with a glass rod. This procedure, however, is totally unnecessary with my reagent, and I have never used it. Probably the water and hydrochloric acid present help materially to bring about quick solution of the residue. I do not know whether the authors "add slowly a strong solution of potassium hydroxide (10 to 12 normal) until the maximum colour is developed" to each residue they are dealing with; but I should have thought that the best plan would be to make a special KOH solution containing, say, 600 grms. per litre, add some gradually from a measuring cylinder to a diluted residue of 1 cc. standard KNO₃ solution, after the phenolsulphonic acid has been added, and note the amount required to give the maximum colour. Then mark the bottle with that amount, and always add the same measured quantity in each case.

A MODIFIED EXPLOSION EUDIOMETER.

By F. H. CAMPBELL, M.Sc.

THE form of explosion eudiometer described below having been found to be much more convenient than that ordinarily used, and being novel as far as the author has been able to ascertain, it is considered advisable to give an account of it. As is shown in Fig. 1, the alteration consists simply

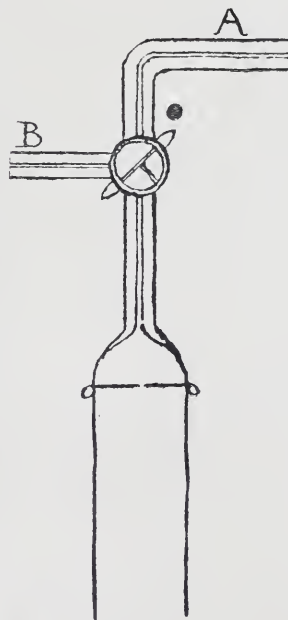


FIG. 1.



FIG. 2.

in the addition of a three-way capillary tap. In Fig. 2 the general arrangement of the apparatus adopted when it is desired to demonstrate the proportions in which various gases unite by volume is shown.

Rubber rings are placed round the eudiometer in convenient positions, the tap is opened, and the air expelled by sinking the tube in the mercury; the tap is then closed, and the tube raised until the upper ring is at the level of the mercury in the cylinder. The tube A is then con-

nected to a gas generator or holder, a Kipp's apparatus in which hydrogen is being formed, for example; the tap is turned so that A and B communicate, the gas is allowed to stream through B until the air is displaced from the connecting tubes; the tap is then turned, and gas admitted to the eudiometer until the desired volume has been collected. The eudiometer is again raised until the second ring is level with the mercury in the reservoir, after which the second gas is admitted.

Should any gas remain after the explosion it can easily be obtained and examined by opening the tap, and sinking the eudiometer.

Though primarily designed for lecture demonstrations the apparatus may be used for exact work, graphite being used as a lubricant in place of vaseline, &c.

The eudiometer has the following advantages over the ordinary form:—

1. The tube can be completely filled with mercury, the mercury drives the air out in front of it, and no bubbles stick to the sides.

2. The volumes of the gases used can be exactly controlled.

3. The residual gas, if any, can be collected in a pure state and tested.

4. Each experiment occupies five or six minutes only, so that—

5. A series of experiments can be carried out during the same lecture, allowing of the demonstration of the validity of Gay Lussac's Law, whatever the proportions of the gases used, and the damping effect of excess of either gas on the violence of the explosion.

Working Men's College,
Melbourne, Victoria.

NEW ORGANIC COMPOUNDS OF NITROGEN.*

[By Prof. MARTIN O. FORSTER, D.Sc., Ph.D., F.R.S.]

It may be stated without fear of contradiction that the most versatile form of elemental matter is nitrogen. Rivalled only by argon and its associates in reluctance to take part in chemical action, its entrance into combination with other elements leads to interesting forms of activity in great profusion. Union with hydrogen in different proportions, for example, produces ammonia, hydrazine, and hydrazoic acid, three highly reactive substances having characteristics which stand in marked contrast with one another. If oxygen be brought into the system, hydroxylamine, nitrous acid, and nitric acid may be mentioned as typical materials capable of entering into chemical changes of the most diverse order.

Organic derivatives of nitrogen, however, present an even greater display of individuality. Prussic acid, the alkaloids, nitroglycerine, gun-cotton, celluloid, artificial musk, lyddite, indigo, the azo-dyes, hæmoglobin, and the enzymes are a few of the conspicuous nitrogen compounds which suggest themselves in this connection, and a survey of their activities would justify a reference to nitrogen as—

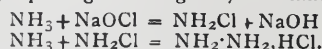
"An element so various it seems to be
Not one, but all Hermetic Art's epitome."

It is not the occasion, however, to discuss the foregoing materials, my present purpose being rather to deal with some new organic derivatives of nitrogen which, although not associated with any important industrial development, nevertheless display properties of considerable interest to chemists.

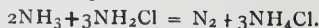
The extraordinary inertness of elemental nitrogen has been already mentioned, and the underlying cause of this feature is the tenacity with which two atoms of the substance remain in combination with each other. But in circumstances which will be explained later, three atoms of nitrogen may be brought into and maintained in com-

bination, the resulting complex being known as the triazo-group. It is a remarkable fact that although, as has just been seen, nitrogen is distributed among naturally occurring substances almost as widely as carbon itself, there is no recorded example of a triazo-compound being obtained from natural sources. Clearly then, the union of atoms in the triazo-group is not among those marriages which are made in Heaven.

That being the case, it becomes necessary to consider the materials and processes which underlie the synthetical production of triazo-compounds. Proceeding from ammonia, and replacing one of the hydrogen atoms by an amino-group, diamide, or hydrazine, is produced, but although discovered by Curtius in 1887, the method by which he prepared it is of historical interest only, it having been left to the ingenuity of Raschig, as recently as 1907, to accomplish the production of this substance by a simple and inexpensive process. This consists in first replacing an atom of hydrogen in ammonia by an atom of chlorine, and then, by direct action of more ammonia on the resulting chloramine, replacing the halogen by an amino-group:—



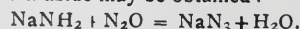
The new process illustrates in remarkable fashion the effect which physical condition may exert on chemical change. Although chloramine and ammonia may act together as already shown in a constructive direction, an alternative, destructive course is open to them, which is accelerated if the viscosity of the liquid is diminished:—



Thus Raschig was able to increase the yield of hydrazine by increasing the viscosity of the solution with addition of glue, whilst the undesirable effect, namely, liberation of nitrogen, was shown to follow the addition of acetone.

Just as ammonia may be doubled on itself to produce diamide or hydrazine, the latter might be expected to allow one of its hydrogen atoms to be replaced by another amino-group and furnish triamide, or triazane. This, however, has not been accomplished, and there is evidence to suggest that such a substance would be most unstable. Whenever attempts are made to add another nitrogen link to the chain of two atoms in hydrazine, the terminal atoms of the three-link chain are found to have combined with one another, forming an enclosed association or ring of atoms. This is the triazo-group, and its simplest known form is the compound with hydrogen called azoimide, or hydrazoic acid, HN_3 . The latter name emphasises the first point of interest in connection with the triazo-group. Whereas the simpler compounds of nitrogen with hydrogen, namely, ammonia and hydrazine, are both strong bases, forming very stable salts with acids, azoimide is a well-defined acid, forming salts with bases including ammonia and hydrazine themselves, the products then having composition expressed by the curious formulæ, N_4H_4 and N_5H_5 . Another salt, that with ferric iron, provides a very delicate test for hydrazoic acid, the red colour being noticeable in solutions containing only one part per million.

Hydrazoic acid, discovered in 1890, also by Curtius, may be shown by experiment to follow an attempt to add another atom of nitrogen to hydrazine. Whilst the action of nitrous acid on ammonia causes both atoms of nitrogen to be liberated in elemental form, $\text{HNO}_2 + \text{NH}_3 = \text{N}_2 + 2\text{H}_2\text{O}$, hydrazine is converted by the same agent into hydrazoic acid, $\text{HNO}_2 + \text{NH}_2\cdot\text{NH}_2 = \text{HN}_3 + 2\text{H}_2\text{O}$. This process, however, is not adapted to the production of hydrazoic acid or its salts in large quantities. Two methods are available for this purpose. One of these, due to W. Wislicenus (1892), consists in passing a current of dry nitrous oxide over shallow layers of powdered sodamide at about 200° , and by means of certain modifications good yields of sodium azide may be obtained:—



A later method, elaborated by Stollé and Thiele working independently (1908), is based on the experiment just

* A Discourse delivered before the Royal Institution, May 5, 1911.

mentioned, namely, the action of nitrous acid on hydrazine, but instead of using free nitrous acid, an ethereal nitrite, such as ethyl or amyl nitrite, is employed. These materials, in presence of alkali, transform hydrazine into sodium azide, the yield being excellent; and this discovery has resulted in the commercial production of that salt, which may now be purchased at less than 40s. per pound—



The free acid is a dangerous and disagreeable substance to manipulate. When free from water, it condenses to a colourless mobile liquid, which boils at about the same temperature as ether (37°); but although harmless looking, it is a frightful explosive, and requires but slightly elevated temperatures for the display of this property. Moreover, the vapour is extremely poisonous, and when inhaled in even trifling quantities causes distressing headache; it is, in fact, a powerful protoplasmic poison, its activity in this direction being comparable with that of prussic acid. As might be expected, therefore, its effect on the blood-spectrum is immediate and pronounced.

To chemists, however, the most conspicuous property of hydrazoic acid is the resemblance it bears to the halogen acids, a solution containing only one part per million giving a faint turbidity with silver nitrate. The resulting silver azoimide, in common with other hydrazoic salts of heavy metals, is dangerously explosive, but the salts of the alkali metals may be handled without risk. The latest recruit to the metallic azoimides is radium azide, described by Ebler about six months ago, and utilised in attempts to prepare metallic radium, which appears to follow the decomposition of radium azide by heat, just as barium azide may be shown to yield the metal when deprived of nitrogen. Pursuing the analogy between the triazo-group and the halogen atoms, a study of the refrangibility and dispersion of light by organic triazo-compounds deserves attention. The following measurements have been carried out by Philip, and show that while the mean increment of refraction for an atom of bromine is 8.93, that of the triazo-group is 8.91, and whilst the atomic dispersion of bromine is 0.35, the increment traceable to the azoimide nucleus is 0.36.

	Contribution of N ₃ -group to	
	Refraction.	Dispersion.
Ethyl triazacetate	8.74	0.35
Ethyl α-triazopropionate	8.87	0.36
Ethyl β-triazopropionate	8.86	0.37
Ethyl bistriazacetate	9.07	0.38
Triazoethyl alcohol	8.97	0.35
Bistriazethane	8.98	0.36
Benzylazoimide	8.85	0.35
Contribution of N ₃ (mean) ..	8.91	0.36
Contribution of Br.	8.93	0.35

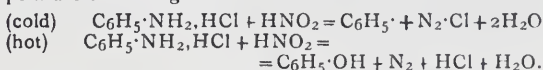
Moreover, on comparing the temperatures at which a number of typical triazocompounds boil with the constants for halogen derivatives having similar structure, it appears that the triazo-group exerts an elevating effect considerably greater than that of chlorine, somewhat greater than that of bromine, and approximating to that of iodine. Furthermore, it has been shown by Philip that the introduction of a triazo-group into a molecule of acetic acid has an effect on the strength of the acid which is rather less than that due to a bromine atom and rather greater than that caused by an iodine atom.

	Dissociation constant.
Acetic acid	0.00018
Iodoacetic acid	0.00075
Triazacetic acid	0.00093
Bromoacetic acid	0.00138
Chloroacetic acid	0.00155
α-Triazopropionic acid	0.00086
α-Bromopropionic acid	0.00108

Thus the physical evidence supports the chemical indications, and serves to classify the triazo-group as a complex radicle with a strong family resemblance to the halogens.

Bearing this resemblance in mind, it was natural to anticipate the possibility of constructing a composite molecule in which the azoimide nucleus is united with one atom of a halogen, for example, chlorine, just as molecular chlorine is composed of two similar atoms. Such a synthesis has been lately accomplished by Raschig (1909), by the interaction of hypochlorous and hydrazoic acids, $\text{HClO} + \text{HN}_3 = \text{ClN}_3 + \text{H}_2\text{O}$, but the union between the two components is very easily broken, and chloroazoimide is highly explosive.

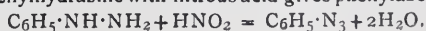
Proceeding now to study the behaviour of the triazo-group when placed in an organic environment, it is necessary first to examine the operations by which typical organic azoimides may be prepared. Although too numerous to be even summarised on the present occasion, some points in connection with the changes involved require attention. We have seen that the action of nitrous acid on ammonia sets free completely the nitrogen present in both materials. If, instead of ammonia there is taken its benzene derivative, aniline, in the form of the hydrochloride, nitrogen becomes added to that of the aniline, and although it is true that the product, when heated, gives up all its nitrogen just as ammonium nitrite does, the intermediate compound is perfectly stable at the temperature of melting ice:—



This intermediate compound and related substances are among the most important, from both practical and theoretical standpoints, known to chemists. They are called diazonium salts, and their discovery, with that of many remarkable changes undergone by them, is due to Peter Griess (1858). It is not the least illuminating feature of Griess's work that the study of the diazo-compounds, underlying as it does the immensely valuable coal-tar colour industry, was pursued by its author while employed as chemist in a well-known firm of brewers, to whose particular undertaking the work in question had no application; such far-sighted encouragement of apparently useless research for its own sake is an object lesson which is not, unhappily, without value even in these days.

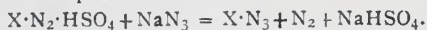
Fascinating as are the problems, solved and unsolved, within the boundaries of diazo-chemistry, it would be inappropriate to encroach on them this evening, but the diazo-compounds forming a natural stepping stone to the triazo-derivatives, it is relevant to draw passing attention to one recent application of their activity. The great class of artificial colouring matters known as aniline dyes depend largely, though by no means exclusively, upon the process known to chemists as "coupling." If an aromatic base which has been treated with nitrous acid is added to one which has not been so diazotised, combination usually takes place in such a manner that a derivative of azobenzene is produced, and in the factory or laboratory coupling is effected with aqueous solutions maintained at zero to avoid decomposition of the diazo-group. A class of substances recently described by Morgan and Micklethwait, however, make it possible to administer the diazo-complex in a solid form, thereby greatly facilitating a demonstration of the coupling process; on mixing a few decigrams of toluene-*p*-sulphonyl-*p*-phenylenediazoimide with the same quantity of *α*-naphthylamine, adding a few cc. of pyridine, and diluting the solution with absolute alcohol, concentrated hydrochloric acid develops an intense permanganate coloration.

We now arrive at the stage immediately preceding the organic triazo-compounds. Just as hydrazine itself, when treated with nitrous acid, gives hydrazoic acid or azoimide, so phenylhydrazine with nitrous acid gives phenylazoimide,



its production in this way gives the first indication of its properties, for unlike aniline and phenylhydrazine, which are bases, phenylazoimide is a neutral substance, resembling its haloid analogues, chlorobenzene, bromobenzene, and iodobenzene.

Although phenylazoimide was first brought to light by Griess in 1866, the subject of triazo-chemistry lay dormant until the discovery of hydrazoic acid by Curtius in 1890. Since that time the province has been a flourishing one, and the number of triazo-compounds which have been prepared and studied by Curtius and his pupils constitute an imposing section of nitrogen chemistry. It is principally with the acid azides, substances in which the triazo-group plays the same part as chlorine in benzoyl chloride, that the investigations of Curtius have been concerned, and it is noteworthy that some of the earliest syntheses of polypeptides were effected by him simultaneously with Emil Fischer through the agency of these compounds; in the subsequent development of this field, however, the azide process gave way to the linking up by chlorides, as adopted and elaborated by Fischer. The method by which Curtius prepared his acid azides is really an adaptation of the change by which hydrazoic acid itself is obtainable from hydrazine, namely, by the action of nitrous acid upon the hydrazides of the respective acids, and it may be stated in general terms that any derivative of azoimide may be produced in this way provided the corresponding derivative of hydrazine is available; but this is the case only in certain classes of compounds, and the preparation of aromatic azoimides is best accomplished by a process due to Noelting, which consists in adding sodium azide to the diazonium sulphate:—



The remarkable instability of the diazonium azide, upon which this reaction depends, recalls that of the diazonium iodide, following which the iodine atom may be introduced into a benzenoid compound, and incidentally offers one more analogy between the triazo-group and a halogen. Moreover, resemblance to the haloid elements is suggested not only by this method of introducing an azoimide complex into the aromatic nucleus, but also by the circumstances attending its removal. It is well known that a chlorine atom in the benzene ring is so firmly attached that it cannot be removed by hot caustic alkalis, but that if nitro-groups also are present in the ortho- and para-positions, the halogen may be removed quite easily, so that picryl chloride is converted into picric acid by the action of water. Very similar relationships prevail among the substituted azoimides of benzene and naphthalene, from which hydrazoic acid may be eliminated according to well-defined principles.

It is now six years since we were led, at the Royal College of Science, to a study of the triazo-group by the accidental discovery of triazocamphor, a substance which displays properties in some respects novel, and in this connection it gives me the greatest pleasure to acknowledge that the development of the subject has been in a large measure due to the courage and ingenuity displayed in its early stages by my former colleague, Dr. H. E. Fierz. The majority of the new materials differ from those of previous workers in belonging, not to the aromatic series, but to the other great class of organic substances, the aliphatic derivatives. It is with a study of the general behaviour of the triazo-group in the diverse environment afforded by these two classes that we have been concerned, and with this object have prepared azoimides of such simple types as acetaldehyde, acetone, acetic acid, ethyl acetate, acetamide, ethyl alcohol, ethyl ether, substituted malonic acids, the unsaturated hydrocarbons ethylene and propylene, and, lastly, ethylamine. To these have been added certain bistriazo-compounds, namely, those of ethane, acetic ester, malonic ester, and acetoacetic ester. In this latter class the explosive character of the triazo-group has been very prominent; for instance, whilst a drop of ethyl triazoacetate when thrown on a hot plate

merely inflames without detonation, 1:2-bistriazoethane explodes with considerable violence; and this property is particularly noticeable when both triazo-groups are attached to the same atom of carbon, 1:1-bistriazoethane continuing in existence only a few minutes after isolation, when it disappeared with a deafening explosion. Another characteristic feature of these materials becomes evident when their vapour is inhaled, the experience of pleasure in an ethereal odour being quickly followed by a throbbing sensation at the base of the forehead often accompanied by palpitation of the heart. Whilst, however, the derivatives of benzene and naphthalene usually acquire an odour of anise by the introduction of the triazo-complex, the perfume connected with such substances as the azoimides of ethyl acetate, ethyl alcohol, acetone, ether, and acetic acid, is quite devoid of the anise character, and is, indeed, much fainter than that of the parent compound in each case.

The method by which these aliphatic azoimides have been prepared is extremely simple. It depends on interaction of the corresponding halogen derivative with sodium azide; for example,—



and appears to be almost general. The reaction has been lately applied to the nitrosochlorides of pinene, dipentene, the limonenes, and terpineols, and it has been further found that the azoimide complex may be exchanged for the nitroxy-group in nitrosates, such as those of amylene and dipentene.

(To be continued)

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 2nd, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Colour Blindness and the Trichromatic Theory of Colour Vision. Part III. Incomplete Colour Blindness." By Sir W. DE W. ARNEY, K.C.B., F.R.S.

The first part of the paper shows how if an equation be formed by rays in known position in the spectrum to match a white, by normal vision and by the colour blind, the two can be compared together without special reference to the luminosity of the matched white. The luminosities of all the rays are known in the one case, and only two in the second, and from the two matches the unknown deficiency of colour sensation can be calculated. Owing to the fact that large quantities of their white can be mixed with the colours without being detected by those incompletely colour blind who have a small factor for one of their sensations, a very false interpretation of their colour blindness might be arrived at by the method described above. If, however, the luminosity of the composite white and the matched white be carefully equalised, a full determination of the colour deficiency can be arrived at by treating the equation somewhat in the manner described in Part II. of this same subject, when a true result is obtained.

The latter part of the paper dealt with colour equations made from the rotation of discs, and it is shown that reliable results can be obtained from their use, so long as the sensations stimulated by the pigments in the light in which they are viewed are known in amount. The method of ascertaining the sensation composition of the pigments, and of the light used for their illumination, is described. When once these are known, no further appeal to the spectrum is required. The author recommends the use of a white light passing through a yellow substance, such as chromate of potash solution, as a viewing light, in which only the red and green pigments are required in the inner disc, the blue not being wanted. The "grey" match becomes thus much brighter and is easier to read.

"The Iridescent Colours of Birds and Insects." By H. R. A. MALLOCK, F.R.S.

In this note reasons are given for the view that certain forms of brilliant coloration, which occur in the feathers of birds, and in the scales and integuments of insects, are due to interference, and are of the nature of the colours of thin plates.

Walter, in 1895, in Germany, and quite recently Michelson, in America, have written on this subject, and, basing their opinions on the behaviour of polarised light when reflected from the colour-producing surfaces, conclude that the colours are due to selective absorption and reflection, and are akin to those reflected from certain aniline dyes and from metals.

The reasons against this view and in favour of interference are—(1) that when any of these natural colour-producing structures are penetrated by a fluid having the same refractive index as that of the material of which the structure is composed, the colour disappears; (2) when the refractive index of the fluid is less, the colour does not disappear altogether, but changes towards the red; (3) which is perhaps the most important, under mechanical pressure the colours first change towards the red, and then (as the pressure increases) disappear. These results are what might be expected from a structure which produces interference, and it is difficult to reconcile them with any other hypothesis.

The note is founded on observations extending over many years on examples of this class of colour production, taken from a considerable number of orders and genera, both of birds and insects, and the methods of examination employed are shortly described.

"Behaviour of the Infusorian Micronucleus in Regeneration." By K. R. LEWIN, B.A.

"An Enquiry into the Influence of the Constituents of a Bacterial Emulsion on the Opsonic Index." By A. F. HAYDEN, M.B., and W. P. MORGAN.

"Morphology of Trypanosoma gambiense (Dutton)." By Col. Sir DAVID BRUCE, C.B., F.R.S.

"Factors in the Interpretation of the Inhibitive and Fixation Serum Reactions in Pulmonary Tuberculosis." By A. H. CAUFELD.

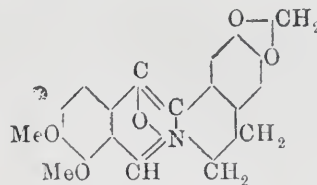
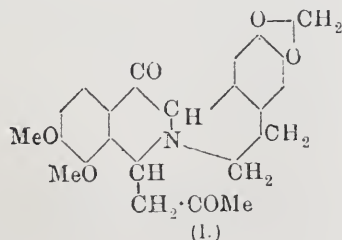
"Preliminary Report upon the Injection of Rabbits with Protein-free (Tuberculo-) Antigen and Antigen-serum Mixtures." By A. H. CAUFELD.

CHEMICAL SOCIETY.

THE following completes the abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions* :—

214. "isoQuinoline Derivatives. Part VI. neoOxyberberine." By FRANK LEE PYMAN. (*Trans.*, 1911, 1690).

Berberineacetone, $C_{23}H_{23}O_5N$, yields on oxidation with permanganate in aqueous acetone neoxyberberineacetone, $C_{23}H_{23}O_6N$ (I.). When this substance is hydrolysed by dilute acids, salts of neoxyberberine, $C_{20}H_{17}O_5N$ (II.), are obtained :—



The phenolbetaine constitution assigned to neoxyberberine is supported by its general properties, and particularly by its behaviour with methyl iodide, when methoxyberberinium iodide is produced. neoOxyberberine is readily reduced to tetrahydroberberine, and its chloroform solution suffers spontaneous oxidation in the air, with formation of 1-keto-6 : 7-methylenedioxytetrahydroisoquinoline and 1-ethyl hydrogen hemipinate.

215. "The System : Palmitic Acid-sodium Palmitate." By FREDERICK GEORGE DONNAN and ALBERT SIMPSON WHITE. (*Trans.*, 1911, 1668).

The compositions of the solid and liquid phases in equilibrium with each other have been determined over the temperature-range 60—82°. The solid phases consist of three series of solid solutions. No pure acid salts appear to separate as stable phases in the region of temperature and concentration investigated.

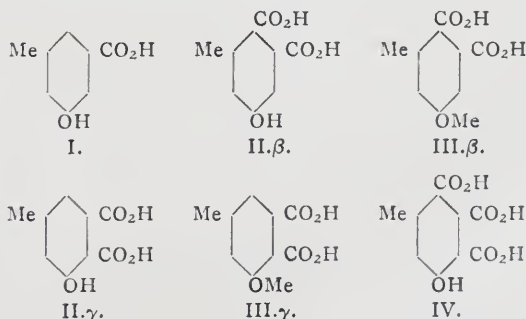
216. "The β -Chlorocinnamic Acids." By THOMAS CAMPBELL JAMES. (*Trans.*, 1911, 1620).

The various methods for the preparation of the two β -chlorocinnamic acids have been examined, and the proportion of the isomerides obtained in each case determined. A quantitative separation is possible by means of the barium salts in aqueous solution; the *allo*-acid is readily, and the other sparingly, soluble.

The transformation of the acid melting at 132.5° into that melting at 142° under the influence of heat and of sunlight, and the rate of elimination of hydrogen chloride by means of alkali, establishes the acid melting at 132.5° as the *allo*-isomeride.

217. "Substances Related to Cochenillic and Carminic Acids. Part I. Synthesis of the Methyl Ether of β - and of γ -Coccinic Acids." By ANDREW NORMAN MELDRUM. (*Trans.*, 1911, 1712).

Starting with 5-hydroxy-*m*-toluic acid (I.), the author has synthesised two methoxyphthalic acids which are related to cochenillic acid (IV.). One of them is the methyl ether (III. β) of β -coccinic acid (II. β), whilst the other is the methyl ether (III. γ) of an unknown substance (II. γ), which may be called γ -coccinic acid.



218. "The Synthesis of Hydrocarbons at High Temperatures." By JOHN NORMAN PRING and DORIAN MACE-FIELD FAIRLIE. (*Trans.*, 1911, 1796).

A method has been applied for the detection of synthesis of traces of hydrocarbons produced when p

carbon, in the form of a rod, is heated electrically in an atmosphere of hydrogen. At 1200°, and at pressures from 10 to 60 cm., carbon combines with hydrogen to give methane and ethylene, the rate of formation of the latter being about 1/100 that of the methane. No acetylene could be detected by this method at this temperature (1200°).

Measurements made of the rate at which acetylene and ethylene react with hydrogen to give methane show that sufficient time was not allowed in the above experiments for any large interaction of ethylene or acetylene with hydrogen to occur, so that the formation of the hydrocarbons must have been direct.

At 1400°, and at pressures between 10 and 40 cm., methane and acetylene are obtained, the rate of formation of the latter being about 1/10 that of the former.

At 1650° methane, ethylene, and acetylene are obtained, and, as at higher temperatures, the quantity of ethylene is about twice that of the acetylene.

Palladium, in contact with the carbon, was found to assist catalytically the formation of methane to the same degree as platinum, whilst silicon had no appreciable effect.

The presence of a highly charged electric field surrounding the carbon made no appreciable difference to the rate of formation of methane at temperatures between 1200° and 1600°, so that no complication is produced in the reaction by ionisation from heated carbon.

The formation of ethylene, which has not before been observed at these low temperatures, can just be detected by the special method employed for the analysis, at 1200°, and at 1400° it is comparable with the methane formed.

219. "2:2'-Dibromodiphenyl and 2:2'-Dichlorodiphenyl." By JAMES JOHNSTON DOBBIE, JOHN JACOB FOX, and ARTHUR JOSIAH HOFFMEISTER GAUGE. (*Trans.*, 1911, 1615).

The authors have studied the action of cuprous bromide on the tetrazonium salt derived from 2:2'-diaminodiphenyl. They show that, according to the conditions, the products are, on the one hand, mainly diphenyleneazone, (C₆H₄N)₂, and carbazole, and, on the other, a small amount of 2:2'-dibromodiphenyl, large quantities of carbazole, and traces of diphenyleneazone.

2:2'-Dibromodiphenyl crystallises from alcohol in long colourless prisms, melting at 81°. Diphenylene is formed by the action of sodium on the substance dissolved in dry ether (*Trans.*, 1911, xcix., 683). Fluorene results from the action of sodium on a mixture of 2:2'-dibromodiphenyl and methylene dibromide.

2:2'-Dichlorodiphenyl, formed similarly to the dibromocompound, crystallises from light petroleum in nodular masses of crystals, melting at 59°.

220. "The Absorption Spectra of various Chlorine and Bromine Derivatives of Benzene and of Toluene as Vapours, in Solution, and in Thin Films." By JOHN EDWARD PURVIS. (*Trans.*, 1911, 1699).

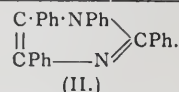
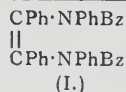
The general results are that: (1) each vapour possesses a considerable number of bands which can be divided into groups, regulated by the type and number of the side-chains; (2) alcoholic solutions of the substances give considerably fewer bands, and of a different type from the vapour bands; and (3) the bands observed through very thin films are not unlike the solution bands, and differ only in position.

221. "The Effect of Heat on a Mixture of Benzaldehyde-cyanohydrin and Aniline." By ARTHUR ERNEST EVEREST and HAMILTON MCCOMBIE. (*Trans.*, 1911, 1752).

The following substances were found to be produced in this reaction:—

1. After half-an-hour's heating a quantitative yield of anilinophenylacetoneitrile, CN·CHPh·NHPh, is obtained. This substance has not been prepared previously without the use of either a sealed tube or a catalyst.

2. If the heating is continued for forty-eight to ninety-six hours, dibenzoyldianilinostilbene (I.) is formed:—



3. Mixed with compound (I.) was generally 1:2:4:5-tetraphenylglyoxaline (II.). These two compounds were separated by taking advantage of the insolubility of the former in hot ether.

4. α-Keto-β-anilino-αβ-diphenylethane was sometimes isolated in the reaction.

5. Benzanilide was also found to be present.

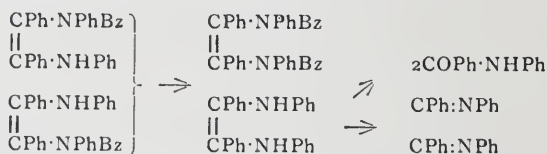
Dibenzoyldianilinostilbene can be decomposed quantitatively by potassium hydroxide, yielding the monobenzoyl compound and benzoic acid.

The constitution of these two compounds (the dibenzoyl and the monobenzoyl) was established by the decompositions undergone by monobenzoyldianilinostilbene (a) in solution, (b) on heating.

A solution of benzoyldianilinostilbene undergoes atmospheric oxidation, yielding benzanilide and benzoylaniline:—



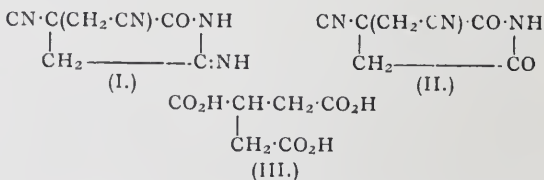
Benzoyldianilinostilbene when heated undergoes decomposition, regenerating the dibenzoyl compound, and forming benzanilide and benzildianil in addition:—



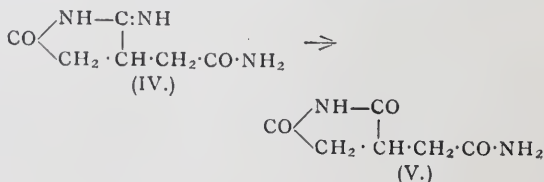
Benzoyldianilinostilbene is strongly yellow, but a colourless modification has been prepared. By spectroscopic means it has been established that the salts are derived from the colourless variety, and not from the yellow form.

222. "The Formation and Reactions of Imino-compounds. Part XVI. Reactions leading to the Formation of Tricarballic Acid." By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE. (*Trans.*, 1911, 1684).

Cyano-amides having the nitrile group in the γ-position readily pass into imino-derivatives of the five-membered ring; thus the condensation of iodoacetoneitrile and the sodium compound of cyanoacetamide gives the imino-compound (I.), from which the imide (II.) can be produced by the action of acids, and ultimately tricarballic acid (III.):—



The imino-compound (IV.) is produced when the sodium compound of ethyl cyanoacetate is condensed with iodoacetamide. It yields the imide (V.) when treated with acids, and tricarballic acid on further hydrolysis:—



There is no tendency to form either the three- or the four-carbon ring through the agency of the imino-group.

223. "Composition of the Essential Oil of *Myrica Gale*, L." By SAMUEL SHROWDER PICKLES. (*Trans.*, 1911, 1764).

The oil of *Myrica Gale*, L. (bog myrtle, sweet gale, &c.) required for this investigation was distilled from specimens of the plant collected in Argyllshire. Two separate consignments of the raw material contained different proportions of leaves and twigs, and the oils obtained in the two cases consequently varied somewhat in character. The oil obtained from a sample consisting mostly of leaves was pale yellow. It had a pleasant, herb-like odour, and possessed the following chemical and physical characters:—

Yield of oil on air-dried material, 0.203 per cent; D_{15}^{15} 0.912; n_D^{20} 1.426; acid value = 4.0; total saponification value = 23.2; ester value = 19.2; saponification value of acetylated oil = 56.4.

The constituents of the oil were found to include the following substances:—(1) A crystalline paraffin hydrocarbon, m. p. 63–64°, having probably the composition $C_{29}H_{60}$ (0.75 per cent); (2) free palmitic acid (2.5 per cent); (3) terpenes, including dipentene; (4) cineole; (5) esters of fatty acids; (6) a mixture of alcohols of high boiling-points; and (7) a sesquiterpene.

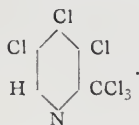
The cineole and terpenes together constitute approximately 50 per cent of the oil.

224. "Trimercuridiethylammonium Nitrite." By PRAFULLA CHANDRA RAY and JITENDRA NATH RAKSHIT.

By the interaction of ethylamine and mercuric nitrite, both dimercuriammonium nitrite and trimercuridiethylammonium nitrite are obtained; a large excess of ethylamine favours the formation of the latter. This new compound is of interest as being the alkylsubstituted product of mercuriammonium nitrite.

225. "The Chlorine Derivatives of Pyridine. Part XI. Some Interactions of 3 : 4 : 5-Trichloropycolinic Acid and of its Derivatives." By WILLIAM JAMES SELL. (*Trans.*, 1911, 1679).

One of the chief compounds obtained by the chlorination of α -picoline has the constitution represented by the formula:—



This substance has been shown to produce by the action of sulphuric acid—besides 3 : 4 : 5-trichloropycolinic acid and 3 : 4 : 5-trichloropyridine already described—a small quantity of another substance, most probably 4 : 5-dichloro-3-hydroxypicolinic acid. This substance is resolved by heat into the corresponding dichlorohydroxypyridine. The above hexachloropycoline also reacts with alcoholic sodium hydroxide, and yields 3 : 5-dichloro-4-hydroxypicolinic acid, also resolved by heat into the corresponding dichlorohydroxypyridine, isomeric with the above dichlorohydroxypyridine.

It is also shown that 3 : 4 : 5-trichloropycolinic acid yields, when heated with ammonia at 140°, 3 : 5-dichloro-4-aminopycolinic acid, which, when heated, gives 3 : 5-dichloro-4-aminopyridine.

Further, the last-mentioned compound forms, when the amino-group is replaced by the hydroxyl group, the same dichlorohydroxypyridine as is obtained by the action of alcoholic sodium hydroxide on the original hexachloropycoline and heating the dichlorohydroxypicolinic acid thus produced.

226. "An Application of Kirchhoff's Equation to Solutions. (A Contribution to the Thermodynamic Theory of Solubility)." By ROBERT TAYLOR HARDMAN and JAMES RIDDICK PARTINGTON. (*Trans.*, 1911, 1769).

It is shown that a general differential equation of van't Hoff may be integrated by an application of a theorem of Kirchhoff relating to the influence of temperature on heat of reaction. The resulting equation gives the solubility of a substance in terms of the absolute temperature and three constants: $\log S = A - B/T - C \log T$, and is shown to agree very closely with the results of experiment.

227. "The Aerial Oxidation (Rusting) of Metals." By WYNDHAM ROWLAND DUNSTAN and JOHN RICHARD HILL. (*Trans.*, 1911, 1835).

In continuation of previous work, the authors have investigated the cause of the inhibiting effect of certain substances, for example, alkalis, potassium dichromate, &c., on the rusting of iron and other metals. It has been found that this effect is in all cases the result of the establishment of a "passive" condition of the metal, during the continuance of which the metal does not rust. The effect persists long after the metal has been removed from the inhibiting solution and carefully washed with water. Contact of passive iron with certain salts or dilute acids, including carbonic acid, more or less rapidly destroys the passivity, and rusting ensues. The authors point out that many of the results recently quoted in support of the carbonic acid theory of rusting are invalidated by the facts now recorded, and further evidence is produced in favour of the conclusion maintained in previous papers, that the presence of carbonic acid is not essential to the rusting process.

The authors record the results of experiments showing that the electrolytic theory of rusting cannot be maintained. It is also shown that other metals besides iron exhibit the phenomena of rusting, and are also capable of assuming the passive state.

228. "The Passivity of Iron and Certain other Metals." By WYNDHAM ROWLAND DUNSTAN and JOHN RICHARD HILL. (*Trans.*, 1911, 1853).

The authors find that the passive state of iron is induced by solutions, in many cases by dilute solutions of a number of salts, such as potassium dichromate, chromate, iodate, chlorate, ferrocyanide, and also by alkalis and alkaline salts, and that, besides iron and metals of the iron group, other metals, including magnesium, lead, zinc, and copper, are also capable of assuming the passive state under the same conditions. Passivity is destroyed more or less rapidly by contact with solutions of certain salts, such as sodium chloride, and also dilute acids, including carbonic acid. It can also be removed by scratching or brushing the surfaces of the passive metal, as well as by other mechanical means.

The destruction of passivity by sodium chloride solution does not take place unless oxygen is present, and the effect is electrolytic, resulting in a slight electrolysis of the salt. In the absence of air, it is found that passivity is not destroyed by sodium chloride or by certain other salts.

The evidence obtained points strongly to the conclusion that passivity is the result of the formation of a film on the surface of the metal. The results of experiments show that this film probably does not consist of "physically" altered metal or of a gas film. The passivity of iron is destroyed by heating in a vacuum to 400°, and disappears when passive iron is heated in hydrogen to 240–250°, at which temperature it is known that magnetic oxide of iron is reducible by hydrogen. The observed facts point to the conclusion that "passivity" is probably the result of the formation of a solid film of oxide on the surface of the metal. It has not, however, been hitherto recognised that certain metals, and especially iron, are capable of oxidation through cold dilute alkaline solutions.

229. "The Reactivity of Ketones towards Iodine and the Relative Rates of Tautomeric Change." Part II. By HARRY MEDFORTH DAWSON and HARRY ARK. (*Trans.*, 1911, 1740).

Further measurements have been made of the rate of tautomeric change of dialkyl ketones and substituted acetophenones. The experiments were made in 40 per

cent alcoholic solution with 0.1 molar sulphuric acid as catalyst, and iodine as speed indicator.

The rate of change of the symmetrical dialkyl ketones diminishes with increase in the number of carbon atoms in the alkyl group. The data for methyl propyl and methyl isopropyl, methyl butyl and methyl isoalkyl ketones, show that substitution of the normal isoalkyl group reduces the reactivity of the ketone by about 25 per cent. The reactivity of methyl *tert.*-butyl ketone, in which the butyl group represents an inactive radicle, is only about two-fifths as great as that of the corresponding normal ketone. Substitution of a hydrogen atom of the phenyl group in acetophenone by a negative atom or group leads to a reduction in the rate of tautomeric change, and similar substitution of one of the hydrogen atoms of the methyl group appears to prevent the change from taking place.

230. "The Photochemical and Thermal Interaction of Chlorine and Carbon Monoxide." By DAVID LEONARD CHAPMAN and FRANK HOUGHTON GEE. (*Trans.*, 1911, 1726).

The authors have continued the investigation of the inhibition observed in photochemical changes when certain impurities are present in very small amounts. The substances which hinder the photochemical interaction of carbon monoxide and chlorine are those which act as inhibitors towards the action of chlorine on hydrogen under the influence of light. The effect of oxygen on the former change has been investigated quantitatively. The thermal union of chlorine and carbon monoxide is homogeneous in character under the conditions prevailing in the experiments performed, that is, when the action proceeds in glass vessels and the area of glass is not extremely large in comparison with the size of the vessel in which the change takes place. The most important conclusion drawn from the results is that the afore-mentioned inhibition is limited to the photochemical change: the inhibitors in question have no influence on the thermal change. This fact was established by measurements being made of the rate of union of chlorine and carbon monoxide in the light and in the dark, at a temperature of 315°, both in the presence and in the absence of nitrosyl chloride. When nitrosyl chloride was present, the rate of union was the same in the dark as in the light; but when it was absent, the rate of union in the light was the greater, the rate of union in the dark being the same as that observed when nitrosyl chloride had been admitted to the mixture.

231. "Decomposition of Dry Ozone." By DAVID LEONARD CHAPMAN and HERBERT EDWIN JONES. (*Trans.*, 1911, 1811).

Ozone desiccated by long exposure to phosphoric oxide, and ozone dried by contact with concentrated sulphuric acid, decompose at the same rate under the same conditions. From this result, and from the results obtained in a previous research by the same authors (*Trans.*, 1910, xcvi., 2463), the inference is drawn that ozone can revert to oxygen without the intervention of any other substance.

232. "The Absorption Spectra of the Isomeric Hydrazones and Semicarbazones of Camphorquinone." By FREDERICK RUSSELL LANKSHEAR and ARTHUR LAPWORTH. (*Trans.*, 1911, 1785).

The spectra fall into two sets, suggesting a classification of the compounds into two series which are identical with the α - and β -series into which they were grouped by Forster and Zimmerli (*Trans.*, 1910, xcvi., 2156; 1911, xcix., 478). The points of difference between the two classes are not sufficiently marked appreciably to weaken the case in favour of the view that the relationship is stereochemical.

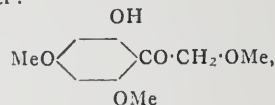
233. "Bimolecular Glycollaldehyde." By NIAL PATRICK McCLELAND. (*Trans.*, 1911, 1827).

The author has investigated the behaviour of bimolecular glycollaldehyde in different solvents and in the state of vapour to ascertain whether it is a kind of acetal formed from two molecules, the hydroxyl group of the one reacting with the aldehyde group of the other and *vice versa*,

or whether the phenomenon is due to molecular association of an unusually intense kind. The conclusion is drawn that the latter is the case, and with the aid of the absorption spectrum of the bimolecular solution it is found possible to make a suggestion as to the character of association in general.

234. "Myricetin." Part III. By ARTHUR GEORGE PERKIN. (*Trans.*, 1911, 1721).

Myricetin hexamethyl ether, $C_{15}H_4O_2(OMe)_6$, which occurs in colourless prismatic needles, melting at 154–156°, is readily prepared by the action of methyl sulphate on the potassium salt of myricetin pentamethyl ether (compare Walliaschko, *Arch. Pharm.*, 1904, ccxlii., 242), or by methylating myricetin with alkali and methyl sulphate. When hydrolysed with alcoholic potassium hydroxide, it gives gallic acid trimethyl ether and 2-hydroxyfisetol trimethyl ether:—



identical with that obtained by Herzig from quercetin pentamethyl ether (*Ber.*, 1909, xlii., 158). Myricetin hexaethyl ether (*Trans.*, 1902, lxxxi., 206) behaves similarly, with production of gallic acid triethyl ether and 2-hydroxyfisetol triethyl ether, which forms prismatic needles, melting at 96–97°. These results confirm the hydroxy-quercetin constitution previously assigned to myricetin.

235. "The Influence of Inactive Electrolytes on the Optical Activity of l-Malic Acid in Aqueous Solution." By CLIFFORD MORGAN STUBBS.

The addition to an optically active solution of various salts and acids which themselves are inactive and do not chemically combine with the active solute, provides a method of varying the solvent in a simple and more or less understood manner. Malic acid was selected as being a well-studied active substance, particularly sensitive to changes in the solvent. For comparative purposes a solution of malic acid of constant strength (20 per cent) was used, to which the various anhydrous salts and acids were added in certain equivalent proportions, and their effect on the specific rotation, mainly for sodium light, determined. The influences observed were, in general, considerable, those for barium and calcium salts being extraordinarily large, and showed the existence of simple relations between the influence of the salt and its chemical nature. The main conclusions are:—

1. The influence of salts is not due to their affinity for water.

2. The influence is mainly a property of the radicles or ions; for salts of strong bases it is an additive ionic property.

3. The property is not due to chemical reaction or adjustment of ionic equilibrium. Ions within the sphere of influence of an active molecule appear to possess the specific power of affecting its degree of asymmetry to an extent depending mainly on their concentration, and not on that of the malic acid. No connection has been found between this power and any known physical properties of the solvent due to the dissolved electrolyte.

4. The divergencies of the alkaline malates (according to Schneider's data) from obeying Oudemans' law appear explicable on the ground of the continued influence of the dissociated, but necessarily adjacent, metal ion.

5. Thomsen's supposed complex-formation between sodium malate and excess of alkali seems explicable on the ground of ionic influence.

236. "New Derivatives of Diphenoquinone and a New Variety of Stereoisomerism." By JAMES MOIR.

By oxidising 4:4'-dihydroxy-3:3'-ditolyl in various ways, ditoluquinone has been obtained apparently in two stereoisomeric forms, namely, a 3:3'- or *cis*-form (red)

and a 3:5'-or *trans*-form (yellow). Both modifications give an orange-brown coloration with sulphuric acid, and are quantitatively reduced by stannous chloride to 4:4'-dihydroxy-3:3'-ditolyl. On mild oxidation, dihydroxyditolyl gives *ditoluquinhydrone*, which forms black needles with a green reflex, and gives a blue coloration with sulphuric acid; the sodium derivative is a bluish purple jelly. *Ditoluquinonedimine* results by oxidising tolidine by Willstätter's method, and is similar to his "diphenquinonedimine," but the properties of both are anomalous, and they are probably polymerides of the true di-imines.

The nitrate of the true *ditoluquinhydronedimine* is easily obtained from tolidine nitrate and ferric nitrate in aqueous solution; it forms opaque blue needles with a bronze lustre, and is hydrolysed by water, the blue solution depositing the *basic nitrate* as a bright blue jelly with a coppery lustre, which can be prepared directly by the action of the theoretical amount of chromium trioxide on tolidine nitrate. When excess of potassium dichromate is used instead, the *dichromate of ditoluquinhydronedimine*, $C_{14}H_{14}N_2 + C_{14}H_{16}N_2 + H_2Cr_2O_7$, is obtained; this is the tetramethyl derivative of the so-called "benzidine chromate," which has recently been shown to be diphenquinhydronedimine dichromate.

Dibromoditoluquinone has been isolated in two modifications by oxidising 5:5'-dibromo-4:4'-dihydroxy-3:3'-ditolyl; it forms scarlet needles with a faint green lustre, and paler lozenges. It gives a scarlet coloration with sulphuric acid, becoming magenta on dilution. Like the parent substance it is practically unaffected by sodium hydroxide. The corresponding *quinhydrone*, $C_{14}H_{10}O_2Br_2 + C_{14}H_{12}O_2Br_2$, is obtained by reducing the quinone with bisulphite, or directly from dibromodihydroxyditolyl by oxidation with ferric chloride in dilute alcohol, or with bromine in acetic acid. It forms needles like graphite, giving a blue coloration in sulphuric acid; the sodium derivative is bright blue, and easily decomposed.

The following new substances are described:—5:5'-*Dibromo-4:4'-dibenzoyloxy-3:3'-ditolyl*, m. p. 239° ; the 4:4'-*diacetoxy*-compound, m. p. 198° ; 5 *bromo-6-hydroxy-m-toluic acid*, m. p. 233° ; 3 *bromo-3'-nitro-4:4'-dihydroxy-3:3'-ditolyl*; 5:5'-*dinitro-4:4'-dihydroxy-3:3'-ditolyl*; and *barium 4:4'-dihydroxy-3:3'-ditolyl disulphonate*.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, November 6th, 1911.

Mr. E. GRANT HOOPER in the Chair.

THE following paper was read and discussed:—

"Deflocculation." By Dr. E. G. ACHESON.

The failure of the author's attempts to utilise American clays as binding materials for incorporation with graphite prepared according to his process led him to consider the difference between residual and sedimentary clays, to which latter class the European clays imported by the United States belong. It appeared improbable that the mere fact of suspension in water could account for the superiority of the latter, and he therefore tested the effect of various organic substances dissolved in water with the idea of simulating the effect of those washed from forests into rivers. It was found that by treatment of clay with dilute solutions of gallotannic acid much less water was required to produce a given degree of fluidity than if water alone were used, and that the tensile strength and plasticity were increased. Systematic experiments confirmed this observation, and it was found that the tannin was removed from solution by the clay. The strength of briquettes formed from clay so treated was more than 200 per cent greater than that of the same clay untreated. The use of straw extract suggested by reading Exodus v. was found to yield equally good results. The clay so treated was called "Egyptianised clay." The beneficial effects of organic

matter on clay were confirmed by other workers who experimented at the author's request, and it was found by microscopical examination that clay so treated became deflocculated. The application of the method of deflocculation, thus indicated, to graphite prepared by the author's process led to the production of two useful lubricants, "Aquadag and Oildag," i.e., deflocculated Acheson graphite suspended in water or oil.

Deflocculation of particles suspended in the deflocculated state is caused by electrolytes, such as acids, salts, alkalis, &c. This fact furnishes some explanation of phenomena such as the formation of mudbanks and deltas at the mouths of rivers. Here the sea-water has an action bringing about "the union of small particles into granular aggregates or compound particles," which is the author's definition of flocculation, deflocculation being the reverse of this. The graphite in the deflocculated condition is found to be in a true colloidal state, the particles being in rapid motion and of a size estimated at 75 millionths of a millimetre, or 3 millionths of an inch, whereas particles of ordinary finely disintegrated graphite are one thousand times as great. The author considers that the particles are actually molecules.

The industrial application of both Aquadag and Oildag as lubricants, and of the former for use with cutting tools, has yielded extremely promising results.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 1st, 1911.

Dr. BERNARD DYER, Past-President, in the Chair.

MR. Horace C. Huish was elected a Member of the Society.

Certificates were read for the first time in favour of Messrs. Shelton Gottlieb Agar, "La Fontaine," Clifton, Guernsey; George Stephen Barton, 8, Exhibition Road, South Kensington, S.W.; Stanley W. Bridge, "Dunsmore," Park Hill Road, Croydon; Richard Victor Briggs, 4, Pollock Street, P.B. 279, Calcutta, India; Francis Clifford Dyche-Teague, 28, King Street, Portman Square, W.; Francis Archibald Mason, the Laboratory, 26a, Great George Street, Leeds; William Bristow Saville, 117, Vassall Road, Brixton, S.W.; George Alfred Stokes, 191, Edgware Road, Paddington, W.

Certificates were read for the second time in favour of Messrs. Ronald Devereux Carty; George Frederick Wesley Martin; and William Keighley Walton.

The following papers were read and discussed:—

"Notes on Shrewsbury and Knapp's Process for Estimating Coconut Oil." By H. S. SHREWSBURY and A. W. KNAPP.

The authors show that the difference between the figures for coconut oil and butter fat by their process (*Analyst*, 1910, xxxv., 385) is about nine times as great as that given by the Polenske method. Further, the Polenske figure depends upon the small percentage of water-insoluble volatile acids that are present, and hence is influenced to a greater extent by treatment of the coconut or palm-kernel oil than the Shrewsbury and Knapp figure, which depends on the bulk of the glycerides.

"Note on a Counterfeit Gold Coin." By HERBERT S. SHREWSBURY.

The author calls attention to a counterfeit sovereign, dated 1861, and uttered at Trinidad.

An analysis of this metal showed it to contain 91.5 per cent of platinum with 5 per cent of antimony and 3½ per cent of copper.

"Examination of Finnish Turpentine." By L. MYDDELTON NASH.

A consignment of Finnish turpentine was found on ex

amination to be normal in all respects except that its close flash was 67° F. instead of from 90° to 100° F. This was proved to be due to the presence of a very small quantity of crude wood alcohol caused by destructive distillation of the wood, the methyl alcohol itself being identified. As Finnish turpentine normally contains a considerable quantity of unpolymerisable matter when examined by Armstrong's process, the author warns against the possibility of regarding as adulterated with benzene or light petroleum spirit such a turpentine as the one described.

"Approximate Estimation of Starch by Iodine." By LESTER REED.

The author describes a method by which the starch, dissolved in glycerin, is precipitated with iodine, the precipitate collected, the iodine expelled by heating, and the residue evaporated and weighed.

"Note on the Gravimetric Estimation of Phosphorus in Milk." By E. HOLL MILLER.

The author shows that during the incineration of milk certain proportions of meta and pyro phosphates are formed, and that unless steps are taken to convert these into the ortho phosphate by boiling with acid, the results of the phosphoric acid determinations made by the ordinary methods are low. The error, although small in the case of milk itself, may easily be very appreciable in the case of condensed milk or milk powders.

"Kobert's Reaction as a Test for Salicylic Acid." By J. McCRAE.

The author describes the reaction obtained by Kobert's reagent (three drops of formaldehyde solution in 3 cc. of sulphuric acid) when added to salicylic acid and a number of other substances such as phenol, catechol, resorcinol, pyrogallol, &c.

"Precipitation of Nickel Compounds and Preparation of Spongy Nickel." By WILSON H. LOW.

The author calls attention to a method by which nickel may be completely precipitated by the combined use of ammonia and hydrazine.

It is pointed out that nickel may be completely precipitated by hydrazine hydrate from solutions containing ammonium salts.

requirements of candidates for the Intermediate and Final Examinations of the Institute of Chemistry have been specially considered. The book gives first of all the preliminary tests employed in the identification of an organic compound, and the tests for the elements, and then special group reactions, by the application of which an unknown substance can be assigned to one or other of the main classes of organic compounds. Individual tests which must be used in order to identify the compound are then given in detail, with the physical constants of a large number of the substances most commonly met with in the laboratory. The arrangement is as systematic as possible, and the hand of the practical teacher who is well acquainted with the actual needs of the average student is revealed on every page.

Guide to the Exhibition of Animals, Plants, and Minerals mentioned in the Bible. London: Printed by order of the Trustees of the British Museum. 1911. (6d.).

THE zoological and botanical parts of this guide are virtually reprints of the labels attached to the exhibits in the Natural History Museum, and the information in it is drawn mainly from Canon Tristram's "Natural History of the Bible." Some illustrations have been added to explain the text. The Director of the Museum has contributed to the guide a short essay on Biblical Minerals and the significance of their Greek and Hebrew names.

Lines in the Arc Spectra of Elements. Arranged in the Order of their Wave-lengths. From Wave-length 7950 to Wave-length 2200. Compiled by F. STANLEY. Published by Adam Hilger, Limited, 75A, Camden Road, London, N.W.

THE wave-lengths are given in Angström units to five figures, and they are arranged in tabular form in four columns—the intensity, the element, and the next prominent line. Some fifty-five elements are included in the list, and room is left on each page for notes. Where it has been possible the "more persistent" (dominant) lines are marked by an asterisk. The figures are said to be taken from the most recent and trustworthy measurements at present available. The front page contains a list of the elements, together with their atomic weights and the range of wave-lengths that are given in the tables.

The book will be found useful by those engaged in arc spectrum work, but the value would have been greatly enhanced if the authorities for the figures given had been quoted.

Winter Specialties. W. Martindale, Manufacturing and Analytical Chemist, New Cavendish Street, W.

THE appropriate illustration of a snow scene on the outside cover prepares one for the long catalogue of devices, medical and other, for combating the many ailments unfortunately prevalent at this season. Considerable prominence is given to various forms of inhalers, and many preparations of "Lysoform," a new antiseptic, are produced. We also note "silky-fibre" handkerchiefs and other manufactures of Japanese paper, a material that is useful for many other purposes than those enumerated in the list.

Potassium Barium Orthosulphantimonate.—Emanuel Glatzel.—Potassium barium orthosulphantimonate, $\text{KBaSB}_4 + 6\text{H}_2\text{O}$, can be prepared by the action of potassium chloride on barium orthosulphantimonate. It forms colourless or white crystals which readily turn brown in air. It shows a very strong tendency to crystallise unlike barium orthosulpharsenate. It is readily soluble in water, and when heated in a test-tube it gives up water and melts to a yellow liquid. Acids decompose the double salt, antimony pentasulphide being formed.—*Zeit. Anorg. Chem.*, lxxii., No. 1.

NOTICES OF BOOKS.

The Ten Republics. By ROBERT P. PORTER. London: George Routledge and Sons, Ltd. 1911. (1s. net).

THIS book, which is the first of a series dealing with the Progress of the Nations, to be published in fifteen to twenty volumes, contains an introductory study of the history, progress, and resources of the ten republics of South America. Succeeding volumes of the series are to take the form of monographs, each devoted to one of the republics. The author has had unique opportunities of obtaining information which is both up-to-date and reliable upon the countries in question, and he has put it together in a very readable form. The book contains suggestions as to the profitable disposal of surplus British capital, and gives a real insight into the economic state of each country, and intending settlers can learn something about the general social conditions from it. It is well illustrated by specially prepared maps.

The Identification of Organic Compounds. By G. B. NEAVE, M.A., D.Sc. (St. Andrews), and I. M. HEILBRON, Ph.D. (Leipzig), F.I.C. London: Constable and Co., Ltd. 1911. (4s. net).

THIS is a distinctly useful little book which the student of organic chemistry will find well worth thorough study after he has had a fair amount of practice in organic preparations, and before he proceeds to research work. The

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other is expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. ciii., No. 15, September 9, 1911.

Magnetic Study of Role of Water in the Constitution of some Solid Hydrates.—E. Feytis.—The author has determined the coefficients of magnetisation of different hydrates of the sulphates of copper, nickel, cobalt, samarium, and gadolinium, and has found that the law of additivity of magnetism can be applied with certainty only in the case of molecules of salts of metals which are strongly electropositive, and which do not give complex salts.

Cementation of Iron by Solid Carbon.—G. Charpy and S. Bonnerot.—In a new series of experiments on the cementation of iron by solid carbon, the authors have found that iron can be kept in contact with solid carbon for thirty-eight hours at 950° without undergoing any trace of cementation, provided that no gas is present which is capable of reacting with the carbon or the metal.

Apparent Reversibility of Vulcanisation of Caoutchouc by Sulphur.—Paul Bary and L. Weydert.—Vulcanised caoutchouc always contains an excess of free sulphur. Obviously if all or part of this sulphur is removed the compound is in unstable equilibrium, and when the specimen is again exposed to the temperature of vulcanisation some of the polyrene sulphide should dissociate. Apparently sulphur is liberated from the polyrene sulphide when the osmotic pressure of the free sulphur is lowered, but the law of mass action cannot be applied to the phenomenon. Caoutchouc becomes insoluble in the usual solvents when it has combined with a certain amount of sulphur, and vulcanisation is always accompanied by depolymerisation.

Hypobromous Amides.—Etienne Boismenu.—The author endeavoured to prepare hypobromites of amides with the intention of transforming them into hypobromous amides by dehydration. But when hypobromous acid acts on amides water is eliminated, and the corresponding hypobromous amide is formed:— $R-CO-NH_2 + BrOH \rightarrow R-CO-NH-Br + H_2O$. In the brominated amides obtained, the bromine preserves its hypobromous character, as seen from its behaviour towards indigo, arsenious anhydride, and potassium iodide. Thus the brominated amides are undoubtedly hypobromous amides. Brominated acetamide appears to be the only one of the series which exists in the hydrated state.

New Derivative of Urea, Chlorourea.—A. Béhal and A. Detœuf.—When a current of chlorine is passed over urea in the cold, or at about 15°, the gas is energetically absorbed, the temperature rises, and the mixture becomes pasty. When not more than one atom of chlorine to one molecule of urea has been allowed to pass, the mass obtained gives a colourless solution in water, possessing a smell like that of hypochlorous acid, and displacing the iodine from iodides. The reaction which occurs is represented by the equation:—



It is impossible to separate the constituents of the mixture by means of ordinary solvents, for they were either both insoluble or both attacked. But the chlorourea can be isolated in a state of purity by dissolving urea in water and passing in chlorine, and cooling with ice. When crystallisation begins, the solution is cooled with methyl chloride, and the crystals are separated *in vacuo*. Chlorourea melts at 71°, undergoing decomposition. It is soluble in water, giving a colourless solution which slowly gives off nitrogen.

It acts on saturated compounds, either as a chlorinating or as an oxidising agent. With unsaturated compounds it gives addition products, either of chlorourea or of hypochlorous acid.

Bulletin de la Société Chimique de France.

Vol. ix.-x., Nos. 16—17, 1911.

Utilisation of Magnetic Field for Determining Constitution.—P. Pascal.—The author has previously shown how the molecular susceptibility of organic compounds can be calculated by rules to which there are a few definite exceptions. The first group of exceptional compounds includes those which are capable of tautomerism. Thus the β -ketonic acids, their ethers, and the β -diketones behave like a mixture of the enol and ketone forms in equilibrium. It may be shown magnetically that the system undergoes orientation towards the enol form under the influence of negative radicles and towards the ketone form under the influence of positive groups. These results have been verified in the case of cyclohexanone and its substitution products. Totally different results are obtained with solid compounds which are capable of tautomerisation. Thus crystalline resorcin behaves like a diphenol, $C_6H_4(OH)_2 \cdot 3$, and in the magnetic field there is no trace of its tautomer. Similarly, phloroglucin behaves like a triphenol.

Rapid Detection of Elements the Sulphides of which are Precipitated by H_2S in Acid Solution.—Emm. Pozzi-Escot.—The precipitated sulphides are treated with HCl. Thus a solution is obtained which contains Pb, Sb, Sn, Cd, and Zn, and a precipitate containing Cu, Mo, As, Bi, Hg, Au, Pt. The solution gives a precipitate with ammonia, containing Pb, Sn, Sb, and a solution containing Cd and Zn. By treating the HCl precipitate with HNO_3 , Cu, Mo, As, and Bi go into solution, and Hg, Au, and Pt remain undissolved. The elements may be further separated by individual tests.

Analysis of Substance containing C, H, O, N.—J. A. Auzies.—The combustion tube is arranged as usual, but the oxide of copper is replaced by plugs of thorinated asbestos or cotton. Thus C, H, and N are oxidised, giving CO_2 , H_2O , and NO_2 . The water is absorbed by a $CaCl_2$ tube, the NO_2 by a titrated HCl solution of cuprous chloride. The coloration of the liquid is proportional to the quantity of NO_2 absorbed; it is destroyed by using a corresponding quantity of a titrated solution of stannous chloride:— $Cu_2Cl_2 + 2NO_2 = Cu(NO_2)_2 + CuCl_2$, $2CuCl_2 + SnCl_2 = SnCl_4 + Cu_2Cl_2$. The carbon dioxide is weighed in a potash tube.

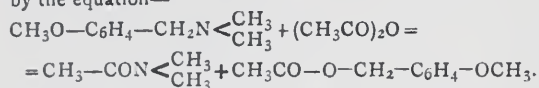
Analysis of Substance containing C, H, O, N, S.—J. A. Auzies.—In this case, after the thorinated cotton, a wad of asbestos is placed, and then PbO_2 . The C, H, and N are determined as before, and the S in passing over the thoria is converted into SO_2 , which is absorbed by the PbO_2 , giving $PbSO_4$. The mixture of unchanged PbO_2 and $PbSO_4$ is dissolved in HCl, and the $PbSO_4$ which remains undissolved is weighed.

Analysis of Substance containing C, H, N, O, S, Cl, Br, I.—J. A. Auzies.—The C, H, N, and S are determined as before. The halogens are absorbed by silver chromate which converts them into chloride, bromide, and iodide. The silver chromate is then treated with ammonia. The residue contains AgI and AgBr. They are separated by a solution of KCN, in which the former dissolves, while the latter is insoluble. The solution obtained on treatment with ammonia contains silver chloride and chromate. It is neutralised with acetic acid, which precipitates them both, and the chloride is dissolved in KCN.

p -Oxybenzylamine.—M. Tiffeneau.— p -Methoxybenzylamine or anisylamine, $CH_3O-C_6H_4-CH_2NH_2$, may be prepared by reducing anisaldehyde by means of sodium amalgam. When it is heated to 130° with two molecules of concentrated HI, and the solution is evaporated to

dryness, the iodohydrate of the demethylated base is obtained. *p*-Methoxybenzylidihydro-isoinol can be obtained by dissolving orthoxylylene bromide in alcohol, and adding a solution of anisylamine in alcohol. On adding HBr the bromhydrate of the base is formed. With acetic acid it yields acetyldihydro-isoinol.

Monomethyl and Dimethyl-*p*-oxybenzylamine.—M. Tiffeneau.—These two bases can be prepared by demethylating the corresponding secondary and tertiary anisylamines. The secondary base, $\text{OCH}_3\text{—C}_6\text{H}_4\text{—CH}_2\text{—NH—CH}_3$, behaves normally towards acetic anhydride, giving an acetic amide which can be heated for several hours with an excess of anhydride without undergoing any transformation, but the tertiary base in the same circumstances splits up, as shown by the equation—



The author believes that this reaction is characteristic of tertiary amines having their nitrogen near a benzylic carbon.

Chlorides of Iridium.—Marcel Delépine.—The three chlorides of iridium, IrCl_4 , $\text{IrCl}_3 \cdot 4\text{H}_2\text{O}$, and IrCl_3 , possess the property of condensing; that is to say, of undergoing transformations into substances of greater molecular complexity. Thus there is a progressive passage from rapidly soluble compounds to less soluble compounds. It is difficult to express these successive condensations in exact quantitative terms.

Compound of Antipyrine and Ferric Chloride.—Ch. Astre and J. Vidal.—A ferric derivative of antipyrine can be obtained by adding ferrous chloride containing hydrochloric acid to antipyrine. After some days it is found that all the ferrous salt has disappeared, and on evaporating the solution crystals of formula $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_3\text{FeCl}_3 \cdot 9\text{HCl}$ are deposited. The substance is very soluble in water and alcohol, and almost insoluble in ether and benzene. The aqueous solution gives all the reactions of ferric salts.

Zeitschrift für Anorganische Chemie.

Vol. lxvii., No. 2, 1911.

Metallographic and Photochemical Investigations of the System Sulphur and Tellurium.—Masumi Chikashigé.—Sulphur and tellurium form no compound with one another. The precipitate obtained with tellurous acid and sulphuretted hydrogen consists of a mixture of tellurium and sulphur. There are two series of mixed crystals. The eutectic consists of them, and occurs at 7 per cent and 109°. The saturated mixed crystal on the tellurium side contains 2 per cent of sulphur. Fused γ -sulphur dissolves up to about 20 per cent of tellurium, while fused β -sulphur dissolves at the most 10 per cent, and solid β -sulphur only 2 per cent. β -mixed crystals are readily transformed into α -crystals by the action of cold or light. The solubility of tellurium in α -sulphur is only about 0.5 per cent. β -Crystals with 0.5 to 2 per cent tellurium are sensitive to light, the rays from $\lambda = 450$ having the strongest action. Mixed crystals with less than 0.5 per cent Te are hardly affected by light.

Hydrothermal Silicates.—Emil Baur.—Hydrothermal silicates may be prepared by exposing aqueous solutions of silicates to high temperatures. The author has prepared many such silicates, and gives tabular statements showing their crystalline characters. Graphic representations of their composition are also given, and the optical investigation of some specimens is described.

Binary Systems of MgCl_2 and CaCl_2 with Chlorides of K, Na, Hg, Pb, Cu, Zn, Sn, and Cd.—Otto Menge.— MgCl_2 and CaCl_2 form no compounds with one another. They yield double salts with KCl and NaCl,

but no compounds with the chlorides of the metals Ag, Pb, Cu, Zn, Sn, and Cd. The diagrams of pairs of salts which contain magnesium chloride and the chlorides of the heavy metals, resemble in their main characteristics those diagrams in which the MgCl_2 is replaced by CaCl_2 . This is not the case in the diagrams in which KCl and NaCl are components. Apparently it may be stated as a general law that if the two metals form no compounds with one another then they yield double chlorides, but not if they do form compounds with one another.

Nickel Superoxide.—C. Tubandt and W. Riedel.—When oxidising agents act on nickelous compounds in absence of free alkali, black precipitates of nickel superoxide are obtained. The action of ozone on cooled solutions of potassium bicarbonate containing nickel salts gives a dark red solution, which appears to be an unstable colloidal solution of nickel superoxide. Weak acids, such as acetic acid, tartaric acid, citric acid, also give colloidal solutions of nickel superoxide. Benedict believed that he had obtained nickelic sulphate by heating nickel superoxide with a concentrated solution of potassium sulphhydrate, but the authors have shown that all the reactions of his supposed nickelic salt are actually those of Caro's acid, and the brick-red powder he obtained is a salt of manganese, present as an impurity. In presence of sulphuric acid nickel superoxide oxidises the lower oxides of manganese to permanganic acid. Attempts to get compounds of trivalent nickel by the anodic oxidation of simple and complex nickel salts, give indications of positive results only in the case of a concentrated sodium bicarbonate solution. The authors have not succeeded in isolating the compound.

MISCELLANEOUS.

Chemical Society.—An Extra Meeting will be held at Burlington House, Piccadilly, W., on November 23rd, 1911, at 8.30 p.m. when Prof. H. B. Dixon will deliver the Berthelot Memorial Lecture.

MEETINGS FOR THE WEEK.

WEDNESDAY, 22nd.—Royal Society of Arts, 8. "Industrial Progress of the United States of America," by J. Douglas, LL.D., &c.

THURSDAY, 23rd.—Royal Society. "On the Iron Flame Spectrum and those of Sun-spots and Lower Type Stars," by Sir N. Lockyer. "Sinhalese Iron and Steel of Ancient Origin," by Sir R. A. Hadfield. "Conductivity of a Gas between Parallel Plate Electrodes when the Current approaches the Maximum Value," by J. S. Townsend. "Spectroscopic Investigations in connection with the Active Modification of Nitrogen—II., Spectra of Elements and Compounds excited by the Nitrogen," by Hon. R. I. Strutt and A. Fowler. "The Less Refrangible Spectrum of Cyanogen, and its Occurrence in the Carbon Arc," by A. Fowler and H. Shaw. "The Monatomicity of Neon, Krypton, and Xenon," by Sir W. Ramsay. "Adherence of Plane Surfaces," by H. M. Budgett. "Resistance to the Motion of a Thread of Mercury in a Glass Tube," by G. D. West. "Distillation of Binary Mixtures of Metals in *vacuo*—Part I., Isolation of a Compound of Magnesium and Zinc," by A. J. Berry. "Analysis of Tidal Records for Brisbane for the Year 1908," by F. J. Selby.

Chemical, 8.30. (Extra Meeting). Berthelot Memorial Lecture, by Prof. H. B. Dixon, F.R.S.
FRIDAY, 24th.—Physical, 5. "Maximum Value of the Electric Stress between Two Unequal Spherical Electrodes," by A. Russell. "Cubical Expansion of Fused Silica," by F. J. Harlow. "Temperature Coefficient of Diffusion," by B. W. Clack. "The α -Particles emitted by the Active Deposits of Thorium and Actinium," by E. Marsden and T. Barratt. "Magnetic Transition-point of Cementite," by S. W. J. Smith, W. White, and S. G. Barker.

ERRATUM.—P. 173, col. 1, for "Hari Juda Bhattachangy, M.A." read "Haripada Bhattacharyya, M.A."

THE CHEMICAL NEWS.

VOL. CIV., No. 2713.

A MOVABLE GAS DISTRIBUTOR.

By PHILIP BLACKMAN.

THIS gas distributor has three brass taps and a brass nozzle. It is of great stability; it will not overturn unless purposely made to do so, on account of the comparatively wide spread of the four supporting feet and their shortness (they are not more than half an inch in height). The

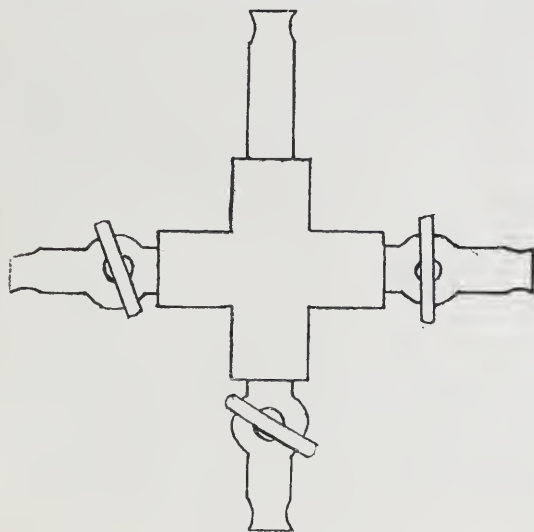


FIG. 1.

(Looking down upon the upper side, showing the positions of the three taps).

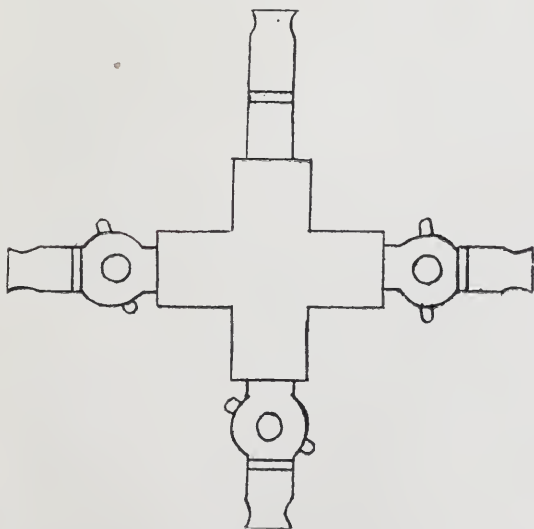


FIG. 2.

(Looking upon the under side, showing the positions of the four supporting feet, marked as double lines).

nozzle can be connected by means of a rubber tube with any gas jet, and the taps with three burners, one or more of which may be used at one time.

This apparatus should be found especially useful where more than one gas jet are not within easy or convenient reach.

It is very strongly made, but should any part get out of order or be damaged it can be very easily replaced.

This apparatus is manufactured and supplied by Messrs. F. E. Becker and Co., 17-27, Hatton Wall, London, E.C.

33A, Princess May Road, London, N.

THE ESTIMATION OF WATER IN SOAP.

By R. M. FITZPATRICK, B.Sc. (Lond.).

THE usual methods in use at present for the estimation of water in soaps often lead to anything but correct results. The method here described suffers from none of the drawbacks of these methods, and as far as tried has given good and consistent results.

One gm. of the sample of soap is weighed from a weighing-bottle into a 200 cc. conical flask, 50 cc. of absolute alcohol added, and the flask warmed until all the soap has dissolved. This is best done by adding a fragment of porous tile, and heating on the water-bath under a reflux condenser.

The solution is allowed to cool somewhat, and filtered through a filter-paper into another 200 cc. conical flask, the first flask being washed out with about 20 cc. of absolute alcohol, so as to convey all undissolved solid on to the filter, which is then washed with absolute alcohol.

The filter-paper with the residue is dried in the steam-oven, cooled in a desiccator, and weighed. The weight of alcohol-insoluble matter in the soap is thus found.

The filtrate is allowed to become quite cold, and 5 grms. of anhydrous sodium sulphate added. The flask is corked, and allowed to stand for at least twelve hours (best overnight). The solution is then filtered into a 200 cc. conical flask which had previously been weighed along with a fragment of porous tile. The sodium sulphate remaining in the flask and on the filter is washed two or three times with warm absolute alcohol.

The alcohol is evaporated off on the water-bath, and the residual soap dried in a steam-oven for fifteen minutes. The flask and soap are cooled in a desiccator, corked, and weighed. From this the weight of anhydrous soap is found. This weight plus the weight of alcohol insoluble residue, subtracted from the weight of soap taken, gives the weight of water. Hence the percentage of water is calculated.

The following are some results obtained in this way, compared with results obtained by difference after all the other constituents of the soap had been estimated:—

Soap.	Water by above method.		Water by difference.	
		Per cent.		Per cent.
1. . . .		25.76		25.51
		25.79		
2. . . .		22.90		22.82
		23.01		
3. . . .		34.13		34.04
4. . . .		30.95		30.88

No. 1 was a textile made mainly from cocoanut oil. (This soap, when dried till the weight was constant, gave a loss of 28.25 per cent.)

Nos. 2 and 4 were special soaps made from cotton-seed oil.

No. 3 was an oleine soap.

A necessary point to observe is that the solution before addition of the sodium sulphate does not deposit any soap jelly. If this happens more alcohol must be added. The total volume of alcohol should not exceed about 110 cc.

Moscow, Russia, October 23, 1911.

DIAMONDS, HOW AND WHEN THEY WERE
MADE BY NATURE.

By ROBERT B. COCKER, R.D.S.

THE accepted theory that diamonds were produced from organic carbon is now shown to be erroneous.

The question is, were diamonds formed before or after organic matter?

The new theory places their origin before, and during an epoch of the earth's history when its atmosphere consisted, for the most part, of carbonic acid gas and carbon monoxide.

The metallic elements of the earth were then in a molten state, liquid and semi-fluid iron flowed freely in various directions, and it must have happened in solidifying that cavities and fissures of various sizes were filled with carbon monoxide and carbon dioxide.

These carbon compounds being enclosed and imprisoned by the surrounding iron, became compressed by the closing together of the sides of the cavities; so that a thousand cubic feet were compressed into the space of, perhaps, one-fourth of a cubic inch, and so highly condensed that the oxygen united chemically with the iron, forming oxide of iron and free carbon, which crystallised by the effect of the enormous pressure produced during the cooling and contracting of the outer matrix.

Diamonds in their native surroundings are found associated with iron; in fact, it is impossible to find a diamond without a trace of iron; when found in river-beds and other places, without blue earth or any ferruginous matter, it proves the immeasurable time that has elapsed since the disintegration of the matrix, which belonged to the molten period of the earth's evolution and millions of years before animal or vegetable carbon existed.

For diamonds to have been produced from organic carbon the whole elements of the earth would again have had to become nebulous, with a temperature of not less than 5527° C.

With the exception of diamonds, carbon does not, and never has existed as a separate element at a temperature below 5527° C. It was certainly one of the first to unite with oxygen and form carbonic acid gas, from which all forms of carbon and their compounds have been directly or indirectly evolved.

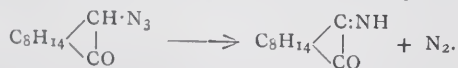
Graphite and coal are accounted for as a result of organic matter; but the origin of the diamond must certainly be placed in pre-organic times.

NEW ORGANIC COMPOUNDS OF NITROGEN.*

By Prof. MARTIN O. FORSTER, D.Sc., Ph.D., F.R.S.

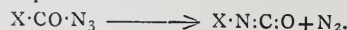
(Concluded from p. 238).

THE various degrees of stability displayed by the azoimide nucleus is the feature which chiefly concerns chemists. Three principal types of decomposition may be recognised. The environment least conducive to stability betrays itself in the liberation of two nitrogen atoms in the elemental form, leaving the third atom attached to the carbon which originally carried all three. This is exhibited by triazo-antipyrine, which loses nitrogen spontaneously at common temperatures, and passes into a bright red azo-compound. Triazoacetone undergoes this change more slowly, but may be stimulated into activity by the catalytic effect of alkali, a property which it shares with triazocamphor—



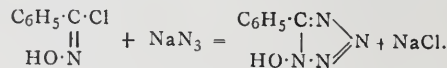
Sometimes excess of alkali must be used and the temperature raised, as in the case of triazoacetic acid, salts of

which, when thrown into hot caustic potash, immediately begin to liberate two-thirds of their nitrogen as gas. The acid azides offer further illustrations of this decomposition, and here the phenomenon is accompanied by a remarkable atomic transformation, first brought to light by Curtius, later studied by Schroeter and others, the denuded nitrogen atom actually changing places with the carbon which formerly carried the triazo-group, with the result that isocyanates are produced:—

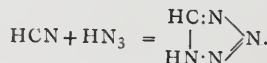


Sometimes this alteration is explosive, as in the case of triazoacetic azide, $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_3$.

The next class of transformation undergone by the triazo-complex is more moderate. It was discovered by Dimroth, and may be described as an unfolding of the three-atom nitrogen ring without loss of the element, all three atoms of which remain in the form of a chain such as occurs in diazaminobenzene; triazen derivatives of this type are, in fact, easily obtainable by the action of alkyl magnesium halides upon organic azoimides, $\text{C}_6\text{H}_5 \cdot \text{MgBr} + \text{C}_6\text{H}_5 \cdot \text{N}_3 = \text{C}_6\text{H}_5 \cdot \text{N} : \text{N} \cdot \text{N}(\text{MgBr}) \cdot \text{C}_6\text{H}_5$. Although some external agency is usually necessary for this type of transformation we have found cases in which it takes place spontaneously. For example, allylazoimide, a colourless mobile liquid when freshly prepared, rapidly changes into a white crystalline solid, consisting of a diazoamino-compound isomeric with the original material, whilst an attempt to prepare benzhydroxamic azide led forthwith to its isomeric transformation product, hydroxy-phenyltetrazole—



More recently, the Italian chemists, Palazzo and Oliveri-Mandala, discovered that fulminic acid and methylcarbamylamine, both highly unsaturated compounds, also are capable of producing this effect on the azoimide nucleus, converting hydrazoic acid into 1-hydroxytetrazole and 1-methyltetrazole respectively, whilst tetrazole itself is obtainable by the interaction of hydrazoic and prussic acids—



The third class of alteration undergone by the triazo-group involves its complete elimination from the molecule in combination with hydrogen, its place being taken by the hydroxy-group. The simplest illustration of this case followed attempts to prepare triazomethylamine, $\text{N}_3 \cdot \text{CH}_2 \cdot \text{NH}_2$, which we found could not be realised because derivatives of that substance display the remarkable property of liberating hydrazoic acid when treated with cold water. The same thing happens when triazotised carbon is associated with a halogen, triazoethylene dibromide, for example, yielding hydrazoic and hydrobromic acids after a few minutes contact with ice-cold water; for this reason it was not possible to realise triazoacetylene, the copper derivative of which might be expected to excel that of acetylene itself in explosibility. More generally, however, this type of decomposition requires the action of alcoholic potash for its completion.

The behaviour of the triazo-group in respect of these three classes of transformation is controlled by its molecular environment, but all organic azoimides have this in common, that they undergo change of the first type—namely, loss of two-thirds the azidic nitrogen, when treated with 80 per cent sulphuric acid, or with various reducing agents. Moreover, they are all extremely sensitive to the action of light. As from time to time the marked analogy between the triazo-complex and the halogens has been emphasised, it should be mentioned that one complete contrast has lately been found. The halogen derivatives of ethylamine are known to part so readily with halogen hydride, that chloroethylamine and bromoethylamine cannot be liberated

* A Discourse delivered before the Royal Institution, May 5, 1911.

from their salts without immediately passing into dimethyleneimine, $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} \text{NH}$, isomeric with the unknown vinylamine or aminoethylene. Salts of β -triazioethylamine, on the other hand, behave like salts of ethylamine itself, and so stable is the resulting triazo-base that it may be distilled from solid potash under reduced pressure without loss of hydrazoic acid.

Many disappointments have occurred in studying the triazo-group, and the most conspicuous one which I have to admit is the failure to produce hexatomic nitrogen; in view of the resemblance between the complex in question and the halogens, and the association of two atoms of the latter in their free molecules, it was to be expected that a new modification of nitrogen might arise by linking together two triazo-radicals. Experiments with this object have failed, and if differently arranged efforts in the same direction are also barren of result, the reluctance of the two nuclei to become united may be regarded as having some bearing on the question of the constitution and transformations of the triazo-group. To aid in the elucidation of this is, indeed, the principal purpose of the foregoing observations, in view of our present ignorance regarding the disposition in space of the atoms or groups which are associated with nitrogen in its organic derivatives. Such disposition or configuration is fairly well understood with respect to carbon, the original views of Kekulé, as developed by van 't Hoff, having stood the test of forty years' unceasing experimentation, but the efforts of chemists to fathom the nature of combined nitrogen, and the arrangements in space of its varying valency directions, have not been so successful. Nitrogen remains a Sphinx among the elements, propounding riddles to the inquiring chemist, although happily, unlike her prototype, she does not annihilate those who fail to solve them.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 9th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"On the Spectrum of Boron." By Sir WILLIAM CROOKES, O.M., For.Sec.R.S. (Will be inserted in full).

"Chemically Active Modification of Nitrogen produced by the Electric Discharge." (II.). By the Hon. R. J. STRUTT, F.R.S.

1. Oxygen destroys active nitrogen, but does not combine with it. Hydrogen has no action.

2. Active nitrogen, in reacting with nitric oxide to form the peroxide, gives the same greenish yellow flame with continuous spectrum which may be obtained by stimulating oxides of nitrogen in other ways.

3. The reaction just mentioned is used to determine the percentage of active nitrogen present in ordinary nitrogen as it leaves the discharge. The result found is about 2.5 per cent, much higher than was formerly supposed.

4. When dilute phosphorus vapour is introduced into glowing nitrogen it does not react at once. It is not until some time after the glow has completely disappeared that the nitrogen gets into a state in which it can react with phosphorus.

5. The glow has a large electrical conductivity, comparable with that of a salted Bunsen flame. The ions are liberated in the glow, not merely carried forward from the original discharge. This ionisation is, as a rule, not very greatly affected when the spectra of other substances, such as metals or cyanogen, are developed by the active nitrogen in the space between the testing electrodes.

6. None of these spectra are visibly diminished in intensity when large electromotive forces are applied to remove the ions.

7. Ozone can in some cases develop metallic spectra when mixed at comparatively low temperatures with the metallic vapour.

"Production of Solid Oxygen by the Evaporation of the Liquid." By Prof. Sir J. DEWAR, F.R.S.

"Gaseous Condensable Compound, Explosive at Low Temperatures, produced from Carbon Disulphide Vapour by the Action of the Silent Electric Discharge." (II.) By Prof. Sir J. DEWAR, F.R.S., and Dr. H. O. JONES.

"Optical Dispersion: a Comparison of the Maxima or Absorption and Selective Reflection for certain Substances." By T. H. HAVELOCK, M.A., D.Sc.

This paper contains a discussion of various wave-lengths associated with each dominant region in a general type of dispersion formula. It is shown how the maxima of absorption and of selective reflection are in general separated from each other and from the wave-length corresponding to the natural vibrations in the molecule. Formulae are obtained for some of these maxima in terms of the constants of the dispersion formula, and are confirmed by comparison with available experimental results. To estimate the magnitude of the differences in question, a numerical study is made of regions of selective absorption and reflection for carbon disulphide, rock salt, and sodium vapour; in particular, for rock salt it appears that the maximum of selective reflection in the infra-red is displaced considerably from the maximum of absorption, and from the dominant wave-length of the dispersion formula.

"Influence of the Solvent on the Position of Absorption Bands in Solutions." By T. H. HAVELOCK, M.A., D.Sc.

According to Kundt's rule, the effect of the solvent is to displace the absorption bands further to the longer wave-lengths the greater the refractive or dispersive power of the solvent. By using a suitable type of dispersion formula this rule is given a definite theoretical expression, and various experimental results are examined from this point of view. Although effects are complicated in general by molecular changes, it is possible to estimate in some cases how much can be ascribed to the operation of Kundt's rule.

"Experimental Investigation of Gibbs' Thermodynamic Theory of Interfacial Concentration in the Case of an Air-water Interface." By Prof. F. G. DONNAN, F.R.S., and Dr. J. T. BARKER.

CHEMICAL SOCIETY.

Ordinary Meeting, October 19th, 1911.

Prof. PERCY F. FRANKLAND, LL.D, F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of the following Honorary and Foreign Members:—Prof. Albert Ladenburg (elected February 2nd, 1888; died August 15th); Prof. Walther Spring (elected January 20th, 1898; died July 17th); Prof. Louis Joseph Troost (elected January 20th, 1898; died September 30th).

It was announced that the Berthelot Memorial Lecture would be delivered by Prof. Harold B. Dixon, F.R.S., on Thursday, November 23rd, 1911, at 8.30 p.m.

Messrs. Irvine Masson, Edwin B. Hughes, H. Horace Ward, and L. O. Newton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Cecil Bescoby, B.A., Guestling, Hastings; Bertram Alfred Bull, Government Road, Nairobi, British E. Africa; Joseph Beauchamp Bull, Bulawayo, S. Africa; Edwin Johnson Charlton, M.Sc., Morannedd, Beaumaris,

North Wales; Barun Chandra Dutt, M.A., Rambogan Cottage, Rambogan, Calcutta; Arthur Josiah Hofmeister Gauge, 2, Ashford Avenue, Hornsey, N.; Sydney Hall, B.Sc., Birley House, Station Road, March; Cyril Vincent Hodgson, 80, Apedale Road, Chesterton; Henry James Hodsman, M.Sc., 2, Richmond Hill, Langley, Birmingham; Alexander Frederick Hogg, M.A., 81, Claremont Road, Forest Gate, E.; Robert Mills, Plantation Uitloft W.C., Demerara, British Guiana; B. Wiswa Nath, 46, Nagappa Modali Street, Komaleswarapet, Madras, India; Thomas Peers Parkes, B.Sc., 22, Dalrymple Road, Brockley, S.E.; David Henry Peacock, B.A., B.Sc., 40, Huddart Street, Bow, E.; B. Venkata Rao, B.A., Bangalore, Mysore, India; Joseph Reilly, B.A., 25, South Circular Road, Portobello, Dublin; Noël Douglas Ridsdale, Ravenscroft, Roman Road, Middlesbrough; William Bristow Saville, 117, Vassall Road, Brixton, S.W.; Bernard Charlie Smith, 62, Filey Avenue, Upper Clapton, N.E.; John Henry Smith, 10, Radnor Street, Swindon; Kapibram H. Vakil, B.A., B.Sc.Tech., No. 5, Santa Cruz, Bombay, India; Harry James Vipond, B.A., Dept. of Agriculture, Pretoria, S. Africa; Ernest Walter Wright, Connaught Club, Seymour Street, W.

Of the following papers, those marked * were read:—

*237. "The Alkaline Condensations of Nitrohydrazo-compounds." By ARTHUR GEORGE GREEN and ERNEST ARTHUR BEARDER.

The authors have studied the action of aqueous alkali hydroxides on 4:4'-dinitrohydrazobenzene, and have ascertained that condensations occur analogous to those which give rise to the stilbene dye-stuffs. A close parallelism is thus indicated between the nitroazo- and the nitrostilbene series.

The blue colour produced when 4:4'-dinitrohydrazobenzene is dissolved in cold alkali hydroxides is apparently due to the formation of the quinonoid salt, $(M'O)NO \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot NO(OM')$, since the original compound is re-precipitated unchanged when the freshly prepared solution is acidified. When, however, the solution is kept at the ordinary temperature for several hours, a slow change of colour from pure blue to violet-blue occurs, with simultaneous precipitation of dinitroazobenzene. The solution after removal of the latter then gives on acidification 4-nitroso-4'-nitrohydrazobenzene, $NO \cdot C_6H_4 \cdot NH \cdot NH \cdot C_6H_4 \cdot NO_2$, which crystallises from acetone in small orange-red cubes having a violet reflex, and decomposes without melting sharply at about 203°. Its alkali salts are violet-blue.

It is rather unstable, and when boiled with neutral solvents or with aqueous alkali hydroxides undergoes further condensation according to the scheme:—

$$NO_2 \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot N \rightarrow \leftarrow N \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot NO_2$$

giving bisnitrobenzeneazo-azobenzene. The latter can also be obtained without prior isolation of the intermediate nitroso-derivative by heating the alkaline solution of dinitrohydrazobenzene for some time at 100° until the disappearance of the blue colour. It forms small orange-red needles, is very sparingly soluble in solvents, and melts at 285–286°.

*238. "The Characteristics and Chemical Composition of some Early Matches." By EDWY GODWIN CLAYTON (see p. 223).

*239. "Experiments on the Walden Inversion. Part VII. Action of Phosphorus Pentachloride and of Thionyl Chloride on Optically Active Hydroxy-acids and Esters." By ALEX. MCKENZIE and FRED BARROW.

The authors have examined the action of thionyl chloride on *l*-mandelic acid, methyl *l*-mandelate, ethyl *l*-mandelate, *l*-malic acid, ethyl *l*-malate, ethyl *d*-tartarate, *l*-α-hydroxy-β-phenylpropionic acid and its ethyl ester, and *d*- and *l*-β-hydroxy-β-phenylpropionic acids. The action of phosphorus pentachloride has been examined in the case of *d*-

and *l*-α-hydroxy-β-phenylpropionic acids and their ethyl esters, and also in the case of *d*-β-hydroxy-β-phenylpropionic acid. The behaviour of the latter acid and its *l*-isomeride towards hydrochloric acid has also been studied.

DISCUSSION.

The PRESIDENT asked Dr. McKenzie whether he had observed any differences in the amount of racemisation occurring according as phosphorus pentachloride or thionyl chloride respectively were employed, and also according as the free acid or an ester respectively were acted on by these reagents.

In reply to the President, Dr. MCKENZIE stated that a Walden inversion is accompanied in the great majority of cases by racemisation, which is often very pronounced. When the action of phosphorus pentachloride and of thionyl chloride towards any one hydroxy-acid (or its ester) is contrasted, it is found that the former has invariably a greater racemising influence than the latter; thus, the crude dextrorotatory phenylchloroacetic acid obtained by the action of phosphorus pentachloride on *l*-mandelic acid is optically active to a much less degree than the crude levorotatory phenylchloroacetic acid obtained by the action of thionyl chloride on *l*-mandelic acid. A similar effect was noted in the behaviour of *l*-atrolactic acid towards phosphorus pentachloride and thionyl chloride respectively (McKenzie and Clough), and there are numerous other instances of the same kind.

In reply to Dr. Forster, it was stated that the method recently described by Darzens (*Comptes Rendus*, 1911, clii., 1601) of replacing the hydroxy-group by chlorine by the action of thionyl chloride on esters of hydroxy-acids in the presence of a tertiary base was not attempted by the authors. By the action of thionyl chloride on ethyl *l*-malate studied by the authors, a satisfactory yield of ethyl *d*-chlorosuccinate with $[\alpha]_D^{19.8} + 32.7^\circ$ was readily obtained, whereas Darzens, carrying out the action in the presence of pyridine, found $[\alpha]_D^{20} + 31.2^\circ$.

*240. "Note on the Preparation of the syn-Aldoximes." By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE.

The method for the preparation of benz-syn-aldoxime discovered by Beckmann (*Ber.*, 1889, xxii., 429, 1531) consists in saturating an ethereal solution of the anti-oxime with dry hydrogen chloride and subsequently decomposing the precipitated hydrochloric with aqueous sodium carbonate.

The authors have found that a much more simple and expeditious preparation can be performed by suspending the finely powdered anti-oxime in cold concentrated hydrochloric acid, and leading in hydrogen chloride to saturation, when, in the case of benzaloxime, the hydrochloride passes into solution, and, in the case of piperonaloxime, the salt is precipitated.

On pouring the resulting solution or suspension into excess of aqueous sodium carbonate, a voluminous precipitate of the syn-modification appears, which can be collected, dried on porous earthenware, and crystallised from benzene. Almost theoretical yields have been obtained in the cases of benzaloxime, piperonaloxime, anisaloxime, and *m*-nitrobenzaloxime.

*241. "The Absorption Spectra of the Nitration Products of Dimethyl-*p*-toluidine." By GILBERT T. MORGAN and ARTHUR CLAYTON.

2-Nitrodimethyl-*p*-toluidine and 3-nitrodimethyl-*p*-toluidine exhibit absorption spectra quite comparable with those of the nitroanilines and nitrotoluidines, the absorption curves showing the broad well-defined band which is characteristic of this series of bases.

2:5-Dinitrodimethyl-*p*-toluidine, which contains its nitro-groups unsymmetrically arranged on either side of the dimethylamino-radicle, gives an absorption curve still showing the characteristic band, but somewhat narrowed and modified. 2:6-Dinitrodimethyl-*p*-toluidine and 3:5-dinitrodimethyl-*p*-toluidine, in each of which the two nitro-

groups are in symmetrical positions with respect to the basic group, give absorption curves differing from the typical form, owing to the almost complete suppression of the absorption band.

The substitution of a third nitro-group in the 2:6-isomeride decreases the symmetry of the molecule, and the product, 2:3:6-trinitrodimethyl-*p*-toluidine, again shows a well-defined absorption band.

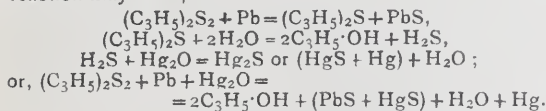
The least symmetrical base examined was 2:3-dinitro-methyl-*p*-toluidine, which contains all its substituents in consecutive positions. This substance gave the typical form of absorption curve with the most persistent band of the series.

The observed difference between the absorption spectra of 2:6- and 3:5-dinitrodimethyl-*p*-toluidines and those of the other bases of this group is due, however, only in part to the symmetrical grouping of the nitro-groups; it is dependent, also, on the presence of the unsaturated basic radicle, for when the basicity is largely destroyed by the replacement of an N-methyl by a nitroso-group, similar spectra are exhibited, as, for example, with 3:5-dinitro-*p*-tolylmethylnitrosoamine, 2:5-dinitro-*p*-tolylmethyl-nitrosoamine, and the corresponding N-nitroamine.

242. "The Action of Allium Sativum or Garlic-juice on Lead and Mercury." By MANINDRANATH BANERJEE.

When the juice of macerated garlic-cruciferæ is triturated with highly impure mercury (containing lead) in a mortar for several hours, a pasty mass adheres to the sides of the mortar, and the mercury remains behind. On adding water to the pasty mass, after removing the mercury, a greyish black precipitate is formed, which, after being collected, dried in the air, and rendered free from minute particles of mercury, proves to be a mixture of lead sulphide (PbS) and a little mercuric sulphide (HgS). The mercury which has been removed, being partly free from lead and other impurities, is repeatedly subjected to the same treatment with garlic-juice, and after three or four hours' rubbing, it is seen to be quite free from lead, and shows all the qualities of pure mercury, when the garlic would no longer act on it.

The sulphur present in the garlic acts on the lead to form lead sulphide (PbS). The higher sulphides present in the oil of garlic, such as diallyl disulphide, propyl allyl disulphide, &c., are reduced to the lower ones, for example, diallyl disulphide is changed into diallyl sulphide or allyl sulphide; this oily liquid mixes with the lead sulphide to form a pasty mass. On adding water, the allyl sulphide and gummy matter present in garlic are dissolved, and lead sulphide is precipitated. The allyl sulphide is partly converted into allyl alcohol, hydrogen sulphide being evolved, which at once attacks the mercurous oxide always present in impure mercury, forming black mercurous sulphide (HgS + Hg) and water. The lead and mercuric sulphides are separated from the mercury, which is thus obtained completely free from lead and mercurous oxide, and is found to be perfectly purified. It has been observed that garlic has no action on pure mercury, and its action on lead alone, even in the finest state of division, is extremely slow, whilst it readily attacks an amalgam of mercury and lead. In the case of diallyl disulphide the reaction may be represented thus:—



243. "Note on *p*-Methoxysalicylaldehyde and its Occurrence in the Root of a Species of *Chlorocodon*." By ERNEST GOULDING and RUSSELL GEORGE PELLY.

In a previous note (*Proc.*, 1908, xxiv., 62) it was shown that the odorous constituent of the roots of *Chlorocodon* sn. is the methyl ether of a dihydroxybenzaldehyde, $OMe\cdot C_6H_3(OH)\cdot CHO$, m. p. 41–42°, but that owing to the lack of sufficient material its configuration had not been established.

A further quantity of the root was subsequently received at the Imperial Institute from Uganda, and was distilled with steam, the yield of the aldehyde amounting in this case to little more than 0.25 per cent, as compared with 0.5 per cent from the earlier sample.

When the compound was fused with potassium hydroxide it furnished either *B* resorcylic acid or resorcinol, depending on the temperature at which the experiment was carried out, thus proving that the substance is *p*-methoxysalicylaldehyde, $OMe\cdot C_6H_3(OH)\cdot CHO$ 4:2:1].

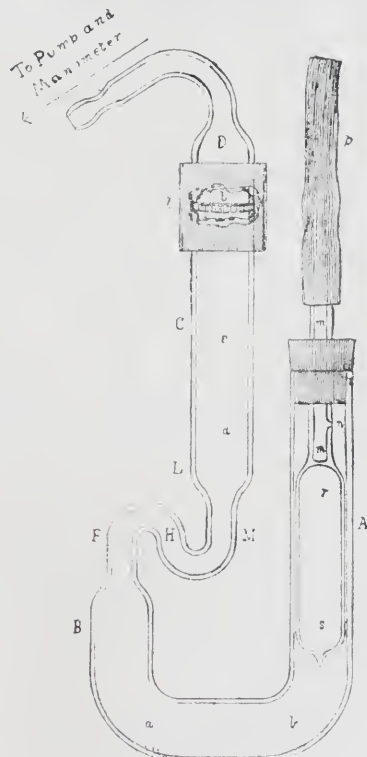
This conclusion has already been reached by Friedländer (*Monatsh.*, 1910, xxx., 879), who obtained the compound by the action of sodium hydroxide on 4-methoxybenzene-2-indoleindigo (formed by the condensation of isatin chloride with resorcinol methyl ether). Friedländer's substance melted at 41°, and was identified with the compound from *Chlorocodon* roots by means of the oxime and phenyl-hydrazone described in the earlier paper (*loc. cit.*).

When an alcoholic solution of the aldehyde (1 mol.) is warmed with aniline (1 mol.), condensation readily takes place, with formation of *p*-methoxysalicylideneaniline, $OMe\cdot C_6H_3(OH)\cdot CH:NPh$, which separates in long narrow lustrous yellow plates, and, after re-crystallisation from alcohol, melts at 67–68°:—

0.4410 gave 23.5 cc. N_2 (moist) at 12.5° and 750 mm.
 $N = 6.22$. $C_{14}H_{13}O_2N$ requires $N = 6.17$ per cent.

244. "A Simple Apparatus for Sublimation in a Vacuum." By HAROLD CHRISTOPHER.

In the course of some recent researches on thioxanthenes it was desired to purify these substances by sublimation in a vacuum. It was found, however, that, owing to the



great density of the vapours, diffusion to the cold part of the sublimation tube was an exceedingly slow process. To overcome this difficulty the idea was conceived of drawing a current of air over the substance, and for this purpose the apparatus illustrated by the accompanying figure was designed. Essentially it consists of a glass tube ABCD,

of which the region *a b* contains the substance to be sublimed, and is heated in an oil- or metal-bath, whilst the limb *c*, into which the vapours of the substance are carried by a current of air, serves as the cooling chamber. In order to prevent the sublimate which collects in the region *d e* from falling back on the unsublimed substance, the tube is constricted and bent, as shown at *F H M*, and to avoid condensation and consequent blocking at this part, the apparatus is immersed in the bath up to the level *L*. The current of air, which is regulated by means of a screw-clip compressing the indiarubber tube *p*, enters the apparatus through the glass tube *m m*, from which it issues by the orifice *n*, and passes down the cylindrical space between the outer wall of the sealed and exhausted tube *r s* and the inner wall of the limb *A* of the sublimation tube. From here it passes over the substance to the condensing limb *c*, and thence through a filter, shown in section at *l*, to the pump. This filter, which is of great importance, the outlet tubes invariably becoming choked if it is omitted, consists of a piece of filter-paper held against the under-surface of a perforated porcelain disk. It rests on the end of the condensing limb, and is held in place by the head *v* and the thick rubber band *t*. Should the tube *r s* be omitted, vortices are formed, and some of the vapour of the substance is carried to the cool part of the limb *A*, where it condenses. It is not essential that this tube should be sealed at the junction with *m*, but it is perhaps preferable, as any contamination of the inside would be very troublesome to remove. If it is sealed it is safer to exhaust it, at least as completely as is possible, with a water-jet pump, since, when in use, it is surrounded by an atmosphere at low pressure and high temperature. Some idea of the amount of air passing may be obtained by inserting a mercury bubbler between the apparatus and the pump. The substance to be sublimed is, of course, introduced through the limb *A*, and the sublimate scraped out of the limb *c*, the head and filter being removed for the purpose.

This device has proved of great utility in the researches alluded to above. The external diameter of the tube employed was five-eighths of an inch, and the total height about 7 inches. The working pressure was usually about 40 mm. (internal), at which a quite sufficiently rapid stream of air was drawn through by the water-jet pump used, whilst the temperature was in the neighbourhood of 200°.

(We are indebted to the Chemical Society for permission to reproduce the accompanying illustration).

245. "Note on the Dehydration of Crystals." By JAMES BRIERLEY FIRTH.

The removal of water of crystallisation from various salts by means of calcium carbide has been described by Irvine Masson (*Trans.*, 1910, xcxi., 851), who finds that in most cases complete dehydration can be obtained, the rapidity of dehydration depending on the vapour pressure of the hydrate.

In the case of copper, zinc, and magnesium sulphates, the final stage is that of the monohydrate.

The author has conducted a series of similar experiments, using phosphoric oxide, and it was found that the above sulphates could be rendered completely anhydrous. The extent of the dehydration was determined by taking the monohydrate, and in all three cases it was further dehydrated by phosphoric oxide. (It is well known that copper sulphate can be completely dehydrated at 50° by concentrated sulphuric acid).

It would appear, therefore, that the apparent stability of the monohydrate, when calcium carbide is used, must be due to the conditions under which the dehydration is carried out.

The decomposition of calcium carbide results in the production of calcium hydroxide. Now it would appear that, if during dehydration any hydrate was formed which had a vapour pressure equal to, or lower than, that of calcium hydroxide, further dehydration would not be possible.

From the following table it will be seen that this is the case with copper, zinc, and magnesium sulphates.

Vapour Pressures at 25° (a).

CuSO ₄ ·5—3H ₂ O	7.0 mm.	
CuSO ₄ ·1—3H ₂ O	4.7 "	
CuSO ₄ ·0—1H ₂ O	0.8 "	(0.5) (b)
ZnSO ₄ ·6—7H ₂ O	13.6 "	
ZnSO ₄ ·1—6H ₂ O	12.8 "	
ZnSO ₄ ·0—1H ₂ O	1.0 "	(0.5) (b)
MgSO ₄ ·6—7H ₂ O	11.5 "	
MgSO ₄ ·5—6H ₂ O	9.8 "	
MgSO ₄ ·4—5H ₂ O	8.8 "	
MgSO ₄ ·1—4H ₂ O	4.9 "	
MgSO ₄ ·0—1H ₂ O	1.0 "	(0.5) (b)
CaO·H ₂ O	0.8 "	

(a) Foote and Scholes, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 1324.

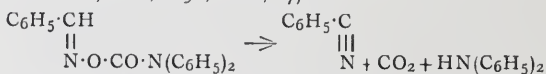
(b) Müller-Ertzbach, *Ber.*, 1881, xiv., 1093; and *Zeit. Phys. Chem.*, 1888, ii., 113.

The vapour pressures of all three monohydrates are very low, and not known very accurately, but they are probably near to that of calcium hydroxide. In all other cases where the dehydration is complete, using calcium carbide, the vapour pressure of the lowest hydrate is higher than that of calcium hydroxide.

The use of phosphoric oxide involves the production of phosphoric acid, and hence secondary reactions frequently occur. In the case of barium chloride the acid reacts with the anhydrous salt, giving a regular stream of hydrogen chloride. This seems to furnish a simple method of preparing fairly pure dry hydrogen chloride. It may be easily done by mixing powdered crystals of barium chloride with phosphoric oxide in a test-tube. In a few minutes hydrogen chloride is evolved, the rate depending on the intimacy of the mixture.

246. "The Diphenylcarbamyloximes." (Preliminary Note). By FREDERICK PERCY DUNN.

The diphenylcarbamyloximes of benzaldehyde and the three nitrobenzaldehydes have been prepared by heating equivalent quantities of diphenylcarbamy chloride and the sodium salts of the "anti"-oximes in dry chloroform or ether. It was found that the same compound was obtained by condensing diphenylcarbamy chloride with the sodium salt of benzantialdoxime as with that of benzsynaldoxime, either by heating or more slowly at the ordinary temperature. Treatment with alcoholic potassium hydroxide gave diphenylamine and benzonitrile, this result showing that the diphenylcarbamyloxime is a "syn" derivative (compare Hantzsch, *Ber.*, 1891, xxiv., 17):—



The syn-diphenylcarbamyloxime of benzaldehyde crystallises in colourless flat needles, decomposing at 163° (Maquenne block). The three diphenylcarbamyloximes of the nitrobenzaldehydes decompose about the same temperature, and all become yellow on exposure to light. As it was found that the sodium salt prepared from o-nitrobenzsynaldoxime was mainly an "anti"-salt, the further investigation of the diphenylcarbamyloximes has been postponed in order to study the metallic salts of the oximes. The author also hopes to prepare the carbamyloximes and the phenylcarbamyloximes.

247. "Some Reactions of Phenyl isopropyl Ketone." By ARTHUR LAPWORTH and VICTOR STEELE.

As isobutyryl chloride is difficult to obtain quite free from propionyl chloride, phenyl isopropyl ketone, prepared by the Friedel-Crafts' reaction, is liable to be contaminated with phenyl ethyl ketone, which may be detected by the formation of β-ketonic esters when the ketone is treated with oxalic, formic, phthalic, and other esters in presence of sodium or sodium ethoxide; the pure ketone does not react at all with these esters.

Phenyl isopropyl ketoxime, which may be used in purifying the ketone, melts at 94° , and appears to exist in one form only, although previous observers have recorded 58° and 61° respectively as the melting-point of the compound.

Whilst inert towards carboxylic esters, phenyl isopropyl ketone is acted on by amyl nitrite in the presence of alcoholic sodium ethoxide, yielding acetoxime, ethyl benzoate, and sodium benzoate, the latter doubtless being formed as the result of the presence of water in the alcohol used.

248. "A New Stereoisomeride of Cyanodihydrocarvone." By ARTHUR LAPWORTH and VICTOR STEELE.

d-Carvone unites with hydrogen cyanide in hot alcoholic solution and in the presence of potassium cyanide, yielding a product isomeric with the nitrile obtained at the ordinary temperature (*Trans.*, 1906, lxxix., 945 and 1819). It melts at 84° , and has $[\alpha]_D^{11} -42.1^{\circ}$ in absolute alcohol; it shows mutarotation in presence of bases, but the equilibrium point attained corresponds with a rotatory power quite different from that reached by the cyanodihydrocarvone first discovered. As both compounds yield pure *d*-carvone on removal of hydrogen cyanide, the existence of four isomeric nitriles derived from *d*-carvone is indicated by these facts, this number corresponding with that theoretically possible.

249. "The Action of Hydrogen Cyanide on Carvone Hydrosulphide." By VICTOR STEELE.

Many ketones which contain an ethylenic linking in the $\alpha\beta$ -position do not form simple cyanohydrins, but first yield saturated β -cyanoketones, which may subsequently be converted, by union with hydrogen cyanide, into hydroxydicyno-compounds.

It was thought possible that in certain cases a cyanohydrin of the $\alpha\beta$ -hydrochloride might be prepared, from which, by hydrolysis and subsequent removal of the elements of hydrogen chloride, the required unsaturated hydroxy-acid might be obtained. As these operations were not found possible, an analogous series of reactions, involving the use of hydrogen sulphide instead of hydrogen chloride, was examined.

The additive compound of hydrogen sulphide with carvone (Varrentrap, *Handwörterbuch d. Chemie*, iv., 688; Kekulé and Fleischer, *Ber.*, 1873, vii., 1088) was mixed with one and a-half times its weight of alcohol and two molecular proportions of potassium cyanide dissolved in water, glacial acetic acid being subsequently added until the whole remained but slightly alkaline. To facilitate interaction, 30 cc. of ether were then added, and the whole left in a corked flask four days at room temperature, when an equal bulk of water was added, and the ethereal solution separated, washed, dried, and evaporated. The residue formed a mass of needles, and was purified by crystallisation from alcohol:—

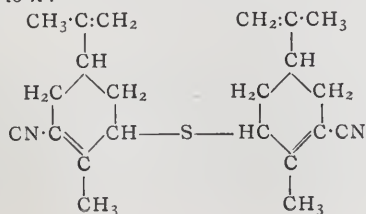
0.1972 gave 0.5422 CO_2 and 0.1414 H_2O . $\text{C} = 75.0$; $\text{H} = 8.0$.

0.1704 gave 11.7 cc. N_2 (moist) at 14° and 760 mm. $\text{N} = 8.08$.

0.2505 gave 0.1657 BaSO_4 . $\text{S} = 9.1$.

$\text{C}_{22}\text{H}_{28}\text{N}_2\text{S}$ requires $\text{C} = 75.0$; $\text{H} = 8.0$; $\text{N} = 7.95$; $\text{S} = 9.09$ per cent.

The compound has therefore been produced by the elimination of the elements of water from the cyanohydrin first formed, and the following formula may therefore be assigned to it:—



The compound dissolves fairly readily in the usual solvent media, with the exception of light petroleum, carbon disulphide, and water; it crystallises from alcohol in flat needles, which melt sharply at 94° . It at once discharges the colour of a solution of bromine in chloroform or of potassium permanganate in acetone:—

0.4062, made up to 25 cc. with absolute alcohol, gave, in a 2 dcm. tube, $\alpha + 0.16^{\circ}$, whence $[\alpha]_D^{12} + 4.92^{\circ}$.

In accordance with the absence of hydroxyl groups, the compound is not altered by acetic anhydride or chloride. It readily loses both hydrogen cyanide and hydrogen sulphide when heated with ferrous hydroxide and alkali, but is stable in the cold.

When titrated with a standard solution of bromine in acetic acid in presence of sodium acetate, 0.5 gm. used up 0.465 gm. of bromine instantaneously, corresponding with 4 atomic proportions of bromine; an additional 0.465 gm. was absorbed in the course of thirty minutes, corresponding with a total quantity of 8 atomic proportions of bromine.

The new dinitrile is partly hydrolysed when heated for three hours with saturated hydrobromic acid, and an acid product, apparently a mixture, is obtained, contaminated with a neutral oil. The acidic portion of the product finally yielded a small quantity of an apparently pure compound which melted sharply at 125° :—

0.1940 gave 0.4770 CO_2 and 0.1443 N_2O . $\text{C} = 67.1$; $\text{H} = 8.2$.

$(\text{C}_{10}\text{H}_{14}\text{:CO}_2\text{H})_2\text{S}$ requires $\text{C} = 67.7$; $\text{H} = 7.7$ per cent.

0.1438 gm. required 7.4 cc. $\text{N}/10\text{-NaOH}$ for complete neutralisation with phenolphthalein as indicator, whence the equivalent is 194; the value calculated for a dibasic acid, $(\text{C}_{10}\text{H}_{14}\text{:CO}_2\text{H})_2\text{S}$, is 195.

The acid is readily soluble in most of the usual media, with the exception of water, carbon disulphide, and light petroleum. It decomposes if heated for a considerable time at 100° , giving a neutral dark coloured oil.

250. "Preparation of the Nitrites of the Primary, Secondary, and Tertiary Ammonium Bases." (Preliminary Note). By PANCHANAN NEOGI.

Small quantities of benzylammonium nitrite (Rây and Datta, *Trans.*, 1911, xcix., 1475), piperidinium nitrite (Neogi, *Ibid.*, p. 1599), and triethylammonium nitrite (Neogi, *Ibid.*, p. 1253) have been obtained by the distillation and sublimation in a vacuum of a concentrated solution of the hydrochlorides of the bases and the alkali nitrites. The actual isolation of these nitrites from the mixtures leads the author to believe that the reaction between nitrous acid and the primary, secondary, and tertiary amines proceeds through the intermediate stage of a nitrite, which decomposes, in the case of a primary amine to alcohol, in the case of a secondary amine to a nitroso-compound, and in the case of a tertiary amine to the original amine.

251. "Studies of Ammonium Solutions. Part I. An Ammonium Electrode." By ROLAND EDGAR SLADE.

When hydrogen containing ammonia is passed over platinised platinum in a solution containing ammonium ions, the platinum behaves as an ammonium electrode. The potential of this electrode at 25° depends on the partial pressures of hydrogen and ammonia and on the concentration of ammonium ions in the solution in the following way:—

$$e = -0.486 - 0.059 \log \frac{p_{\text{NH}_3} p_{\text{H}_2}}{[\text{NH}_4^+]}$$

where $e = e_{\text{electrode}} - e_{\text{solution}}$, and the potential of the normal hydrogen electrode is taken as zero.

Complexes of the form $(\text{NH}_3)_x\text{H}^+$, where x is greater than one, do not exist to any appreciable extent in dilute aqueous ammonia or ammoniacal ammonium chloride solutions, although there is some evidence of their existence at higher concentrations.

252. "The Absorption Spectra of Triketohydrindene Hydrate and Certain Derivatives." By JOHN EDWARD PURVIS.

The results of an investigation of the absorption spectra of triketohydrindene hydrate and its derivatives showed that (1) the colour of the compounds is intimately connected with the presence of ketonic groups; (2) the shade of colour is modified according to the nature of the substituting groups; (3) where another ring is established, there is no selective absorption, and the colour is produced by an extension of the general absorption within the regions of the visible spectrum.

(To be continued)

PHYSICAL SOCIETY.

Ordinary Meeting, November 10th, 1911.

Prof. H. L. CALLENDAR, F.R.S., President, in the Chair.

Prof. SILVANUS P. THOMPSON and Prof. E. G. COKER exhibited two reflecting polariscopes for the study of optical stress in materials. The polariser in each is a sheet of blackened glass at the polarising angle. One has a field 6 in. square, the other 10 in. square. They were designed for the purpose of studying the stresses in objects cut out in sheets of xylonite (celluloid) subjected to mechanical tension. To eliminate the black-cross effect the objects are placed between two quarter-wave plates of mica, having their axes set at 45 deg. Some larger quarter-wave plates of mica were shown, one of them 24 in. in diameter.

Various experiments on surface tension were exhibited by Mr. C. R. DARLING.

In addition to aniline, which has the same density as water at 64 deg., the author has found the following liquids to possess equidensity temperatures:—Anisol at 15, orthotoluidine at 24, butyl benzoate at 48, and aceto-acetic ether at 53. These results have been applied in the production of large drops of liquids, by forming the same in water, when, owing to the slight difference in density between the drop and its surroundings the process is much slower than in the case of a drop falling in air, and may be followed clearly by the eye.

Spherical drops of large size may be produced by taking water in a beaker and one of the above liquids at the temperature of equal density. The liquid is admitted through the stem of a funnel, about 1 cm. diameter, furnished with a tap, the stem terminating below the surface of the water. The liquid sphere forms on the end of the stem, and, if the temperatures be correctly adjusted, may be made to possess a volume of 100 cc. or more.

Large breaking drops, falling vertically, may be obtained if a liquid slightly denser than water is taken. The liquid is allowed to run into water through a tube terminating in a widened portion about 2 cm. in diameter, the flow being controlled by a tap. A pendant drop forms on the end of the tube, which gradually elongates and finally breaks away from the tube, drawing out a neck of liquid, which is afterwards resolved into two or more secondary drops. In the case of small drops breaking from the end of a tube only one small droplet is observed to follow the major portion, and in some cases is not formed. With large drops, however, three droplets of diminishing diameter are generally formed. When the water used is drawn from the tap, orthotoluidine at the temperature of the room may generally be used with satisfactory results; if observed to be of insufficient density, a little aniline may be added.

Large breaking drops rising vertically are obtained when the liquid is less dense than the water, the delivery tube in this case being bent upwards; the drop rises and finally breaks away, usually giving rise to a single droplet. Orthotoluidine at 30 deg., discharged into water at 30 deg., is suitable for this experiment.

Supported drops, or liquid columns, may be obtained by taking a large test-tube containing a shallow layer of water

and pouring into it a quantity of aceto-acetic ether sufficient to form a hanging drop which rests on the bottom of the vessel. The liquid then remains in equilibrium in the form of a column of curved outline surrounded by water, the upper end clinging to the water surface. On adding more water gradually the column becomes thinner and finally breaks, leaving a large drop at the bottom of the vessel and a smaller drop hanging from the surface of the water. Butyl benzoate is also suitable for this experiment.

A quantity of aniline in water at temperatures above 70 deg. alternately rises to the surface and breaks off in the form of a drop which sinks to the bottom of the vessel, the two processes being repeated indefinitely. This is due to the liquid cooling on the surface until denser than the water beneath, when a drop is detached; but in the lower part of the vessel the drop is re-heated until less dense than the water, when it rises to the surface. An investigation of the temperatures of the water and aniline made by means of a thermal junction showed that the temperature of the floating aniline was always about 6 deg. below that of the surrounding water, probably on account of the lower specific heat of aniline (0.52).

When a small quantity of impure orthotoluidine is poured upon the surface of water the floating mass is set into violent agitation, finally breaking up into numerous small spheres. On adding a further quantity a number of globules of circular section are formed, which periodically become indented on one side, so as to resemble a kidney in shape; after which they dart rapidly across the surface. A period of repose follows, after which the globules again become indented and are projected across the surface as before. This procedure is repeated, with decreasing frequency, for two hours or more. When a tranquil state is reached a single large globule is usually observed in the centre of the surface.

A paper on "The Effects of Holes and Semicircular Notches on the Distribution of Stress in Tension Members," was read by Prof. COKER.

The necessities of practical construction lead to a number of interesting cases of stress problems in which discontinuities, like holes and notches, occur in great variety both as regards form and arrangement.

For the experimental determination of stresses in loaded members an optical examination of a model shaped in transparent material has many advantages.

Two cases of primary importance are examined in this way, and the results are compared with those obtained by analysis. The first example relates to the case of a hole in a tension member subjected to a uniformly applied stress, p .

The values of $(p_x - p_y)$, the difference between the principal stresses are readily obtained optically, and they show a fair agreement with the calculated values if the diameter of the hole is not greater than one-quarter of the width of the plate, but beyond this the agreement is not so good. For practical purposes it is important to be able to estimate the maximum stress from the value obtained by assuming that the total load on a tension member is uniformly distributed over the cross-section. A formula based on the relationship found in the experiments takes the form—

$$p_{\max} = \frac{6c^2}{2c^2 + 2c + 1} p_{\text{mean}},$$

where c is the ratio of the width of the member to the diameter of the hole; if c is large compared with unity this reduces to the simple form—

$$p_{\text{mean}} = \frac{3c}{c+1}.$$

In the case of two semicircular notches, arranged symmetrically with regard to their centre line and to the cross-section, there appears to be no exact mathematical solution, but an approximate one has been obtained by Leon, resulting in expressions for p_x and p_y at the minimum section of the form—

$$p_x = \frac{p}{2} \left(2 + \frac{a^2}{r^2} + \frac{a^4}{r^4} \right), \quad p_y = \frac{p}{2} \left(\frac{a^2}{r^2} - \frac{a^4}{r^4} \right),$$

provided that the radius of the notch is small compared with the breadth of the plate.

Experimental determinations of $p_x - p_y$ show that the maximum values agree very well with those of the formulæ for notches having a maximum radius of about one-quarter of the breadth of the member, but the minimum values do not show a very good agreement if the notch has a radius greater than one-eighth of the breadth. The results appear to indicate that the radial stress for large notches is greater than that given by the formula.

For determining the maximum stress from the applied mean stress a formula is proposed of the form—

$$p_{\max} = \frac{12c^3}{6c^2 + 4c^2 + c + 1} p_{\text{mean}},$$

and this shows a fair agreement with the experimental values.

Prof. SILVANUS P. THOMPSON exhibited a large harmonograph for inscribing on a moving ribbon of paper the harmonic movements produced by compounding together mechanically the oscillations of two heavy pendulums.

The recording pencil consists of a glass tube drawn to a fine aperture, in which tube is inserted an ordinary sable-hair paint brush, dipped in ink, so that the mere point of the brush projects through the orifice. He also described his apparatus (shown in operation in the laboratory) for demonstrating the physiological effect of an alternating magnetic field. An alternating electric current with a frequency of 50 periods per second is led into two large copper coils, producing an alternating magnetic field of an intensity of about 10,000 C.G.S. units in the space between the coils. If the head is placed in this space a singular sensation of a flickering bluish illumination is perceived. The effect is greatest if the direction of the lines of force of the field is through the temples.

Prof. Thompson also demonstrated several experiments in acoustics. These were:—(a) A Rubens' tube 15 ft. in length, with a row of small gas flames along it, exhibiting the position of the nodes and ventral segments when the internal gas column was thrown into partial modes of vibration by shrill tones; (b) a Rayleigh flame of peculiar sensitiveness; (c) a dynamical model in glass of the three semicircular canals of the ear. The canals being filled with coloured liquid, and containing model otoliths (made of glass bubbles filled with air), movement of rotation about any one of the three axes sets the liquid in the corresponding canal into relative motion; (d) a set of steel bars for demonstrating the superior limit of audition; (e) a *ton-variable* of Dr. Stern, consisting of a resonant cavity of adjustable volume excited by a gentle air-blast, and graduated to produce any tone between the frequencies of 200 and 400 per second; (f) an adjustable resonator, in which the size of the front opening is altered by use of an iris diaphragm; (g) a new phenomenon in resonance. If a tuning fork is introduced into a tubular resonator having a front orifice just wide enough to admit the two prongs, resonance is observed when the prongs are placed just in the opening. On inserting them deeper the sound ceases, but is again heard if they are inserted still further.

RÖNTGEN SOCIETY.

MR. A. A. CAMPBELL SWINTON, M.I.E.E., the new President of the Röntgen Society, devoted a considerable portion of his Address from the Chair at the meeting on November 7th to a consideration of the question as to whether the second law of thermo-dynamics applied to living organisms. He reminded the Society that this second law, as stated by Clausius, laid it down that it was impossible for a self-acting machine, unaided by external agency, to convey heat from one body to another at a

higher temperature. The law was stated by Lord Kelvin somewhat differently, namely, that it was impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects. It was in this connection that Maxwell propounded his celebrated proposition, in which he supposed that a demon who could see individual molecules might open and close an aperture in a partition dividing a vessel into two separate portions, so as to allow only the swifter molecules to pass from the first to the second, and only the slower ones from the second to the first, in which case, without the expenditure of work, the temperature of the second would be raised and that of the first would be lowered in contradiction to the second law. The belief was gaining ground that this second law, which prevented us by the use of any mere machine from getting mechanical effect from the general stock of heat, did not apply to living organisms at all. There might even exist living things which in some fashion or other did very much what it was the business of Maxwell's demons to do, and extracted the energy they required from the general stock. The interest of this question would be evident to anyone who had studied the so-called Brownian movements which could be perceived by ultra-microscopic methods in finely-divided solid matter, such as particles of colloidal gold suspended in liquid. Without presuming to pronounce one way or another upon the very startling idea that living matter found means, in some cases at all events, of evading the provision of the second law of thermo-dynamics, Mr. Swinton drew attention to the extraordinary consequences that would ensue if such an idea could be established. We should only have to cultivate the right kind of organism in sufficient masses in order to produce the perpetual motion dreamed of by mediæval philosophers. Moreover, there would be nothing lost. The heat that was thus accumulated locally for our needs would dissipate itself again into the common store, as would also the mechanical effects after they had done their work. The unordered molecular motions of which the Brownian movements gave us an indication, and which constituted heat, would merely be directed for a time in the particular manner needful to give us the required power. Life would be the directing force, but it would be a directing force only and would do no work. The prospect afforded us a glimpse of what might perhaps be destined to take the place of fuel a few hundred years hence, when the present supply of fuel was exhausted, and before means had been found to unlock the still greater stores of atomic energy which had already been half revealed in the energy given out by radium and its kindred substances.

ROYAL PHOTOGRAPHIC SOCIETY.

The Traill-Taylor Memorial Lecture.

THE annual Traill-Taylor Memorial Lecture was delivered at the house of the Royal Photographic Society on November 14th by Dr. W. ROSENHAIN, who took for his subject the making of optical glass. He gave an exhaustive description of the process of manufacture, and sketched its brief history from the time that the Swiss, Guinand, a hundred years ago, discovered that by sufficient stirring the striæ which formed in molten glass owing to the different densities of its components, and the consequent difference in their indices of refraction, could be got rid of. In dealing with the purely optical qualities of optical glass, Dr. Rosenhain touched upon the extremely narrow limits of refractive index and dispersion in the glass of the present day. The refractive index of the optical glass now manufactured varied from 1.46 to about 1.7. It was possible to get glass with a refractive index as high as 1.9, but such glass was too sensitive, tarnished too readily, and was of too yellow a tint for practical purposes. If it were carried further than 1.7 the inherent yellow colour of the oxide made its appearance, and the

glass was of no use, for photographic purposes at all events. Then there was the constant known to optics by the Greek letter ν , which in optical glass varied only from 67 to about 30. These were narrow limits. In the mineral fluorite, on the other hand, this constant ν had a value of 95, or 50 per cent higher than the highest obtainable in glass. The diamond, again, had a refractive index much higher than glass was able to give us. The reason why these optical constants could not be approached in the case of glass was because of its tendency to crystallise and its sensitiveness to atmospheric agents. He believed that optical material would be forthcoming which would give them better constants, but such material would not be glass. It would be obtained probably by making artificial crystals of the various minerals possessing the required optical properties. That was distinctly the direction of progress. He himself had succeeded in producing a few crystals of calcite. They were quite small, but they were produced smoothly and regularly. If that line of research were taken up the results would well justify it in the end, and our optical materials would be carried to twice the extent at present available.

Dr. Rosenhain went on to say that the extremely fine optical properties of some of the modern glass rendered it particularly sensitive. It represented a departure from those conditions of manufacture which resulted in the production of stable properties. The result was glass which was too easily injured. Exactly where the line was to be drawn between safety and durability on the one hand and extremely fine optical property on the other, was a matter for each lens maker, who would have to take into consideration the purpose for which the more delicate glass was to be employed and its position in the lens combination. A practical point to remember was that if glass were found damp the moisture should not be rubbed off with a dry cloth. It was better to wash the damp with water and then the surface could be polished afterwards. Some of the decomposition products formed on the surface of such glass were crystalline, and if subjected to dry rubbing would tend to scratch the surface.

NOTICES OF BOOKS.

A Handbook of Organic Analysis, Qualitative and Quantitative. By HANS THACHER CLARKE, B.Sc. (Lond.), A.I.C. London: Edward Arnold. 1911. (5s. net).

It is undoubtedly true that elementary organic analysis is far more difficult than inorganic analysis, and although it does not necessarily follow that it has a greater educational value, there is something to be said for the view that a systematic course of it should be included in the training of every chemist. This book appears to give an excellent course of work on the subject, and its most valuable feature is a very complete and comprehensive table of all the commonest organic substances. Directions are first given for the preliminary examination of an unknown substance, and for the detection of the groups present in it. Then when the nature of the elements and radicles present and the boiling-point are known, all that has to be done is to turn to the tables in which the compounds are arranged in order of their boiling-points under the headings of the groups contained in them. Other physical constants and a few special confirmatory tests are given for each substance, and these should readily lead to its complete identification. Some quantitative work is also described in the book, and a useful section on optical rotation is added.

Famous Chemists. By E. ROBERTS, B.Sc. (Lond.). London: George Allen and Co., Ltd. 1911. (2s. 6d.).

This book contains a number of biographical studies of famous chemists, arranged chronologically, and for the most part only quite short. The selection of subjects has

been made in such a way as to give a good general view of the gradual growth of chemical knowledge from the time of Stahl to the present day. No living chemists are included. The author's biographical and scientific facts appear to be accurate, and he adds many little details of human interest which will serve to make his pictures of the great men vivid and distinctive to his readers; for instance, the story of Berthollet and the Committee of Public Safety is certain to appeal to young students, and it is by no means hackneyed.

CORRESPONDENCE.

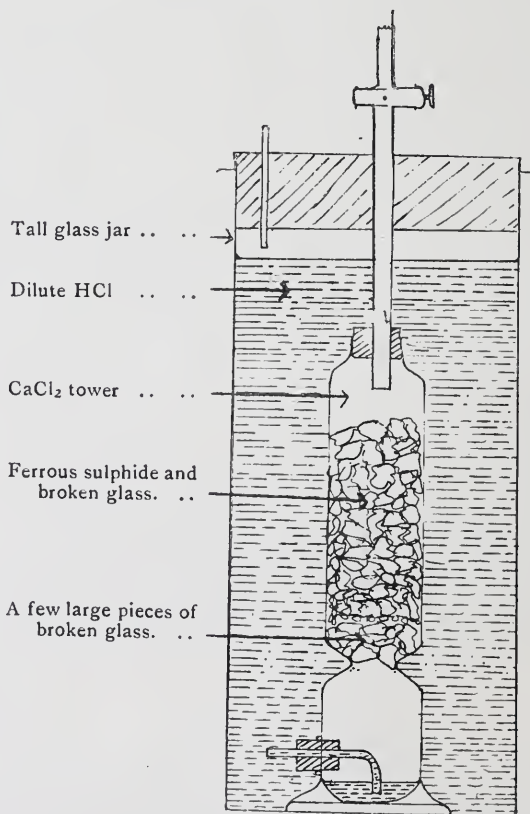
A SIMPLE SULPHURETTED HYDROGEN APPARATUS.

To the Editor of the Chemical News.

SIR,—Seeing in the *CHEMICAL NEWS* (civ., 189) a description of a simple H_2S apparatus, might I point out two serious defects in the same.

1. Gas would be generated before all the acid had passed from the upper beaker, and consequently the gas delivered would be mixed with bubbles of acid.

2. The weight of a thick glass beaker plus the weight of either the iron salt or the acid, would be too great to be



supported by a T-tube. The T-tube would snap at the joint.

The enclosed sketch shows an apparatus of my own design, which I venture to say combines simplicity and cheapness with effective working. The large glass cylinder

contains dilute acid, the drying tower holds a mixture of the iron salt and broken glass. All corks are soaked in wax. The action will be obvious to all readers, being slightly similar to Kipps' principle. I find the combined weight of the tower and iron salt are sufficient to counterpoise the buoyancy produced by the generation of gas.—I am, &c.,

F. T. VERNON.

Chester.

ESTIMATION OF SANTONIN.

To the Editor of the Chemical News.

SIR,—The following method may be used for estimating santonin in preparations containing it.

These preparations contain it usually together with calomel, fat, and insoluble matter.

Where cases of santonin poisoning occur, an estimation of the amount in the stomach and intestines should be made, as well as in the preparation administered.

It is sometimes—on account of its varying solubility in alcohol at different temperatures—found concentrated in dangerous amounts in the medicaments it is mixed with.

Briefly the method is as follows, and, from my experience, is reliable for the estimation of santonin in these preparations:—

A small quantity of the sample is powdered and exhausted with a similar quantity of hot alcohol, which, on evaporation, gives the weight of the santonin together with negligible traces of fat.

Similar treatment, by exhaustion with ether, gives the weight of fat, usually oil of theobroma, when the calomel may be estimated in the insoluble residue.—I am, &c.,

J. C. THOMLINSON, B.Sc., Assoc. Ph.Sc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 16, October 16, 1911.

Volatilisation of Electrodes in Neon Tubes.—Georges Claude. The author has shown in a previous article that the absorption of luminescent gas which is produced in neon tubes is due to the volatilisation or disintegration of the electrodes. The gases obtained by treating the volatilised metal with nitric acid contains, besides neon, a very large proportion of helium. To explain its presence the author put forward three hypotheses:—1. Selective action of the volatilised metal on the helium contained in the neon, but present in such small quantity that it could not be detected by means of the spectroscope. 2. Transformation of the neon into helium. 3. Transformation of the neon into compounds of an ammoniacal nature during the treatment with nitric acid. To test these hypotheses it is necessary to examine the gases furnished by two successive deposits. If the first hypothesis is correct the second deposit should be very poor in helium compared with the first, while if the transformation hypothesis is correct there should be no diminution in quantity. The result of the examination of the gases showed very clearly that the selective hypothesis is true. Ramsay and Collie have come to the same conclusion, employing a different method.

Volatility of Compounds containing Sulphur.—Marcel Delépine.—From the examination of a number of examples drawn from his own work and from that of other

chemists the author has found that the substitution of sulphur for oxygen raises the boiling-point of compounds, except when it takes place in the hydroxyl of water, and of the first members of the series of alcohols, phenols, and acids.

Bulletin de la Société Chimique de France.
Vol. ix.-x., Nos. 18—19, 1911.

Chromic Sulphate and Ions.—Alb. Colson.—The study of aqueous solutions of the normal and isomeric chromic sulphates proves that the osmotic pressure, measured by the cryoscopic lowering, is independent of the constitution of the compounds and of their degree of ionisation. Apparently the osmotic pressure of a concentrated solution of two molecules of $\text{Cr}_2(\text{SO}_4)_3$ remains practically constant, even after it has been made to yield the compounds $\text{SO}_4\text{H}_2 + \text{Cr}_4\text{O}(\text{SO}_4)_5$ by boiling, although the conductivity gradually alters.

Utilisation of Magnetic Field to Determine Composition.—P. Pascal.—The amino dyes, which the author has studied, appear to possess a normal and not a quinonic constitution. In the case of dyes containing hydroxyl and of para-oxazoic derivatives, the existence of two tautomeric forms, azoic and quinonic, seems possible. The quinonic structure is found at relatively high temperatures and when the substance has an intense coloration, while the non-quinonic structure corresponding to low temperatures is characteristic of the less highly coloured form in which these substances exist. In certain cases the two forms may exist together.

Alloys of Nickel and Zinc.—E. Vigouroux and A. Bourbon.—When powdered nickel is fused with zinc in a current of hydrogen the two compounds, Ni_3Zn and NiZn_4 , are obtained. The latter can be isolated by treating with dilute nitric acid melts which contain less than 18.33 per cent of nickel. NiZn_4 is a crystalline non-magnetic powder of density 7.71, which melts at about 850° . Concentrated hydrochloric acid dissolves it even in the cold; dilute hot sulphuric acid acts on it, giving a solution which contains the sulphates of the two metals, and a magnetic powder. Nitric acid rapidly dissolves the compound, nitrous fumes being given off.

Quantitative Separation of Iron and Manganese.—J. A. Sanchez.—If pyridine is added to a neutral or slightly acid solution of a mixture of ferric and manganous salts, all the iron is precipitated as hydrate, and the manganous salt remains in solution. The precipitation of the hydrate is facilitated by warming the mixture of salts before adding the pyridine. In analysing a mineral which contains the metals of the first groups it is best to follow the usual analytical method of separation by means of sulphuretted hydrogen, filter, boil, and oxidise, partially neutralise, and then add pyridine. Zinc is partially precipitated by pyridine. It may be separated by dissolving the hydrate precipitate in HCl and re-precipitating the iron by means of ammonia and ammonium chloride.

Colorimetric Detection of Alcohol in presence of Acetone.—H. Agulhon.—A solution of 0.5 gm. of potassium bichromate in 100 cc. of nitric acid gives a violet coloration with certain easily oxidised organic groups in the cold, and a green coloration on warming. In the cold the reaction is immediately given by aldehydes, primary, secondary, and tertiary alcohols, and all substances containing any of these functions in their molecule—sugars, mannites, fatty oxy-acids. Ketones give the reaction only very slowly, while with aldehydes and alcohols the coloration appears at once. Aromatic ketones give the reaction on warming. Phosphoric acid can be substituted for nitric acid. If 50 grms. of potassium bisulphate are dissolved in 50 cc. of water containing 0.5 gm. of bichromate, a reagent is obtained which gives a green coloration on boiling with all substances containing an uncombined aldehyde or

alcohol function, with ordinary ether, acetic ether, and cyclohexanones.

Products of Hydrolysis of Raw and Pure Pinacone.

—M. Delacre.—When raw pinacone is subjected to hydrolysis followed by fractional distillation, the fraction coming over between 200° and 220° is the most important. When it is subjected to further rectification a mixture is obtained; its composition is approximately that of phorone, $C_9H_{14}O$. From pure pinacoline a liquid of formula $C_9H_{14}O$ is obtained. It is possibly a new isomer of phorone.

Catalytic Dehydration of Secondary and Tertiary Pinacolic Alcohols.—F. Couturier.—When secondary pinacolic alcohol is dehydrated by reduced copper at 300° , pinacoline is obtained. The dehydration of dimethylisopropylcarbinol gives methylisopropylethylene. These results confirm those obtained by the author and M. Delacre, viz., that the action of dry dehydrating agents on pinacolic derivatives tends to give a lateral double bond. Thus the catalytic action of reduced copper resembles the action of dry potash on the halogen derivatives of pinacone and pinacolic alcohol. The results also show that heat does not cause the isomerisation of either of the two pinacolic alcohols when they are undergoing dehydration.

Chlorosulphocarbonic Ethers.—M. Delépine.—Chlorosulphocarbonic ethers can be obtained by the action of carbon sulphochloride on alcohols. The mixture is left for twelve to twenty-four hours at 15° ; then ordinary ether and water are added, meanwhile cooling. The ethereal layer is dried with calcium chloride, and rectified in a current of dry CO_2 . Methyl, ethyl, and propyl chlorosulphocarbonic ethers are pale yellow liquids with a very sharp smell. They fume in air, undergoing oxidation, and are luminous in the dark. The ethyl ether spontaneously undergoes rapid decomposition, giving carbon oxysulphide and ethyl chloride, $Cl.CS.OC_2H_5 = COS + C_2H_5Cl$.

Thionic Ethers.—M. Delépine. Thionic ethers can be prepared by the action of sulphuretted hydrogen on imino-ethers (Matsui), and also by allowing chlorosulphocarbonic ethers to drop into ice-cold organo-magnesium haloid: — $R.C = (NH)OR' + H_2S = R.CS.OR' + NH_3$, $Cl.CS.OR' + XMgR = R.CS.OR' + Mg \times Cl$. The author has prepared nine of these ethers, viz., $CH_3.CS.OCH_3$, $C_4H_9.CS.OCH_3$, $C_6H_5.CS.OCH_3$, $CH_3.CS.OC_2H_5$, $C_4H_9.CS.OC_2H_5$, $C_6H_{11}.CS.OC_2H_5$, $C_2H_5.CS.OC_2H_5$, $C_5H_{11}.CS.OCH_3$, $C_6H_{17}.CS.OCH_3$. They are all pale yellow liquids boiling about 30° higher than the corresponding ether salts. They are insoluble in water and miscible with organic solvents; the five first ethers fume in air, and are oxyluminescent.

Constitution of Nitro-derivatives of Aloins.—E. Léger.—When nitric acid acts on barbaloin and on isobarbaloin, trinitro-oxybenzoic acid and chrysammic acid are formed. The latter is the true generator of the former, and this fact fixes the positions of the NO_2 groups in chrysammic acid, since the oxybenzoic acid is the 2,4,6-trinitro-*m*-oxybenzoic acid.

Atti della Reale Accademia dei Lincei.
Vol. xx., (II.), No. 5, 1911.

Two Forms of Decahydro- β -naphthol.—Luigi Mascarelli.—When β -naphthol is hydrogenated in presence of nickel, a white crystalline mass is obtained which melts at 75° . By fractional crystallisation in petroleum ether it may be separated into two substances, fusing at 75° and 103° respectively. These are two of the four possible isomers of decahydro- β -naphthol.

Phototropism of Hydrazones of Furfural.—L. Santi.—The author has investigated the phototropism of hydrazones of furfural, which are derivatives in which a hydrogen in the α -position is bound to the aldehyde

residue. Thus they contain a pentatomic ring. This ring is found to allow of phototropism, for of the four compounds which the author has prepared phenyl hydrazone, α -naphthyl hydrazone, β -naphthyl hydrazone, and β -tolyl hydrazone—two only (the first) are non-phototropic. Of the other two, β -tolyl hydrazone is only feebly phototropic.

No. 6.

The Angeli-Rimini Aldehyde Reaction.—L. Balbiano.—From the experimental study of the products of the dehydration of the glycol of anetol, the author is forced to conclude that the Angeli-Rimini reaction with Piloty's acid is not only given by aldehydes, but also by some ketones in their enol form.

Basicity of Organic Acids containing Alcoholic Hydroxyls.—G. Calcagni and L. Bernardini. In order to study the effects of introducing an alcoholic hydroxyl group upon the basicity of an organic acid, the authors have determined the electrical conductivity of acids at different dilutions when they are neutralised with varying amounts of a base. Their experiments have extended to glycollic, lactic, α -oxybutyric, and isoxybutyric acids, ammonia being used as the base. In this paper they give details of the experiments performed at five different dilutions and graphic representations of the results.

MISCELLANEOUS.

Announcement.—Mr. Sherard Cowper-Coles has now started private laboratories at 1 and 2, Old Pye Street, Westminster, which are being fitted up especially for electro-chemical and metallurgical work, including electric furnace work, for which a 100 h.p. transformer is being installed.

Institute of Chemistry.—Mr. Bertram Blount, F.I.C., will deliver the second lecture on "Cement" in the Lecture Theatre of King's College, Strand, London, W.C., on Friday, December 1st, 1911, at 8 p.m. *Syllabus*.—General meaning of the term and its limitation in the present discourse. The principal structural cements will be dealt with, and minor adhesives of the workshop will be touched on only incidentally and illustratively, if at all. In practice this delimits the term to calcareous cements. Historical account of the evolution of cements in this limited sense. Cement making is a branch of chemical manufacture. Chemical reactions and physical changes involved in the production of cements and in their setting and decay. Modes of testing, both chemical and physical, the latter including mechanical tests as ordinarily understood. Standardisation of all tests which from their nature are arbitrary, and the device and acceptance of standard specifications. The British Standard Specification as an example. The uses of cements and the errors which may occur from unintelligent application. The causes of failure of structures made with cement. The importance of the aggregate used with cement to make mortar and concrete, and the errors which arise from want of knowledge of its properties. The necessary equipment of knowledge and training for an expert. Physical and mechanical knowledge an essential, in addition to ordinary chemical training. The ignorance now existing of the constitution of cement as produced and when set; the admirable but insufficient work of the past and the consequent opportunities for rigorous research in a subject of exceptional difficulty.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Royal Society of Arts, 8. (Cantor Lecture). "The Carbonisation of Coal," by Prof. Vivian B. Lewes.
WEDNESDAY, 29th.—Royal Society of Arts, 8. "The Efficiency of the Aeroplane," by A. E. Berriman.

THE CHEMICAL NEWS.

Vol. CIV., No. 2714.

A HEIGHT-ADJUSTABLE BURNER.

By PHILIP BLACKMAN.

THE burner consists of a long tube, with a jet at right angles at one end, and a bend at right angles (but in an opposite parallel direction) at the other end, to which the rubber gas connecting tube may be fixed.

It may be clamped by means of an open "boss" to any height upon a retort stand or to the leg of a tripod.

The vertical downward bend of the nozzle will prevent the rubber gas connecting tube from "kinking" as frequently happens when an ordinary burner is raised.



The length of the horizontal part (12 inches or 30 cm.) permits of the easy adjustment in the "boss," so that the jet is exactly under any required spot.

It is strongly made and will not be damaged when screwed up in the "boss."

The upper end of the jet has a screw-thread upon the outside to allow a "star" or "rose" to be fixed when necessary. It is the simplest form of burner.

This burner is manufactured and supplied by Messrs. F. E. Becker and Co., 17, 27, Hatton Wall, London, E.C.

33A, Princess May Road, London, N.

HOFMANN'S METHOD FOR THE DETERMINATION OF VAPOUR DENSITY.

By ALFRED C. EGERTON, Royal Military Academy, Woolwich.

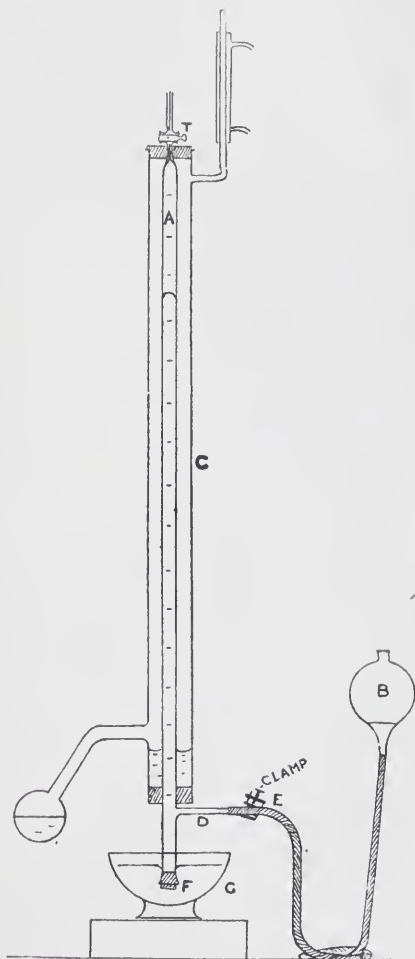
THE most general method of finding the vapour density of a substance is Victor Meyer's method; it is almost universally employed in preference to Hofmann's and Dumas' methods for ordinary laboratory work, while for high temperature work it is well suited.

At the same time, as usually employed, it does not give such accurate results as Hofmann's method. The objections to Hofmann's method as a general method are, firstly, the mercury is acted on by some substances, and, secondly, the trouble which has to be taken to clean, dry, and fill the measuring tube between each experiment; this second objection is undoubtedly that which has caused Victor Meyer's apparatus to oust the older Hofmann method. Ramsay and Young, Thorpe, and others have

from time to time improved Hofmann's apparatus to make it really accurate.

The errors that have to be corrected are the volume alteration due to the expansion of the glass, and the measurement of the pressure which has to be reduced to a column of mercury at 0° C. This last correction is somewhat difficult, as the temperature along the length of the mercury is not uniform, but gets colder towards the bottom of the tube.

Ramsay gets over the difficulty by making a series of measurements at different pressures and volumes, employing a vacuum pump to alter the external pressure on the



mercury in the trough. Thorpe heated the whole of the mercury both in the tube and the trough. However, although accuracy was attained by these improvements and the method was applicable to fine vapour density measurements, the trouble of cleaning, &c., before mentioned still remained.

Cadets at the Royal Military Academy make a few simple determinations of vapour density by Hofmann's method, using an ordinary long graduated tube, wooden bowl trough, and glass steam jacket fitted to the tube.

I had noticed that the laboratory attendant has found difficulty and trouble in re-fitting up the apparatus, and getting the tube quite dry and free from air bubbles. Therefore I have designed the accompanying apparatus to overcome these difficulties.

The graduated measuring tube, A, is fitted with a capillary tap, T, at the top—this should be a good tap lubricated with a non-vaporising rubber grease.

The tap is as close as possible to the cork of the jacketing tube C.

The bottom end of the tube under the mercury in the trough, G, can be closed by a rubber cork, F. A side tube, D, is sealed into the long tube close to the lower cork of the glass jacket.

The side tube is connected by a rubber tube to a mercury reservoir, B. A screw clip, E, is affixed close to the side tube on the rubber tube. The rest of the arrangement is as usual.

For accurate measurement a cathetometer can be used, or a steel or glass scale can be set vertically behind the tube, and fitted at its lower end with a point which can be just set on the surface of the mercury in the trough.

The apparatus is employed according to the following plan:—

1. Fill the trough with clean mercury to the required amount.
2. Fill the reservoir with mercury, the rubber stopper being in the end of the long tube.
3. Lower the apparatus or raise the trough till the bottom of the trough holds in the rubber stopper quite firmly.
4. Raise the reservoir to the top of the tube, opening the tap, and then closing when the mercury fills the tube. Lower the reservoir.
5. Close the screw clip on the rubber tube.
6. Open the rubber stopper, having lowered the trough slightly.
7. Measure the height of the mercury in the tube, and also the barometer.
8. Boil up the jacketing liquid, and let in the small weighed tube through the cork at the bottom of the long tube.
9. When steady read the height of the mercury column and volume of vapour in the tube.
10. Replace the indiarubber stopper, and raising the trough as before on a wooden block to hold it in position; then open the screw clip, raise the mercury reservoir, and open the tap at the top till all the vapour is expelled.
11. Lower the reservoir, close the clip, and lower the trough, and take out the cork; the apparatus is then ready for another determination, which can be made at once.
12. The small bottles can be collected afterwards by opening the screw clip when the mercury runs down to the bottom of the long tube.

The whole point of the apparatus is that the vapour can be expelled while still hot, and the apparatus is then ready for another experiment. The presence of a good tap at the top of the tube does not appear to materially vitiate the results, though a suitable lubricant must be chosen.

The apparatus possesses another merit. I mentioned that in accurate work the expansion of the mercury has to be allowed for, and that this is difficult. With this apparatus it is quite easy. All that is necessary is to use the apparatus like a Regnault absolute expansion apparatus, and construct a curve of heights of column of mercury in hot tube when the height of the cold tube at the ordinary temperature is at definite points on the scale. The two columns having different densities will not be level, as they would be if both were at the ordinary temperature.

In this way, by measuring the expansion of mercury in the tube at different temperatures, one can construct a curve to read off what the height would be at the ordinary measured room temperature, and from that correct to 0°.

The other corrections, such as volume of small tube, vapour pressure of mercury, volume change due to expansion of glass, can be applied as in the usual modification if great accuracy is required.

I have thought fit to publish this slight modification of the apparatus as it may be useful to chemists who require a greater accuracy than Victor Meyer's apparatus will afford, with as little trouble.

Messrs. Gallenkamp supply the apparatus if required.

THE ALLEGED COMPLEXITY OF TELLURIUM.

By AUGUSTUS GEORGE VERNON HARCOURT

and
HERBERT BRERETON BAKER.

THE anomalous position of tellurium in the Periodic System has led to many attempts in recent years to separate it into elements of higher and lower atomic weights. Marckwald (*Ber.*, 1897, xl., 4730), by a laborious process of fractional crystallisation of telluric acid, believed that he had obtained tellurium of atomic weight lower than that of iodine, but on repeating the atomic-weight determinations by a more trustworthy process he arrived at the conclusion that no separation had been effected (Marckwald and Foizik, *Ber.*, 1910, xliii., 1710). Baker and Bennett (*Trans.*, 1897, xci., 1849) described attempts at separation made by seven distinct methods, none of which afforded any evidence that the element was anything but simple. This conclusion was upheld by the work of Lenher (*Jouru. Am. Chem. Soc.*, 1899, xxxi., 1).

More recently, however, Browning and Flint (*Am. Journ. Sci.*, 1909, [4], xxviii., 347) asserted that if tellurium tetrachloride, dissolved in hydrochloric acid, is precipitated by a large excess of hot water, some separation of the element is effected. The work was continued by Flint (*Am. Journ. Sci.*, 1910, [4], xxx., 209). A large quantity of tellurium was purified by precipitation with sulphur dioxide, fusion of the precipitate with potassium cyanide, decomposition of the potassium telluride by air, and distillation of the product in a current of hydrogen. About 1000 grms. of this material were converted into the dioxide, and dissolved in the minimum quantity of hydrochloric acid. This was poured into a large excess of boiling water, and allowed to remain. The dioxide which separated was again dissolved in hydrochloric acid, and precipitated by hot water. When this process had been repeated four times, atomic-weight determinations were made with the material, and gave a mean result of 126.59, and after ten repetitions of the same process the atomic weight obtained was only 124.32. No atomic-weight determinations are given in the paper of the less hydrolysable material.

Since this method of fractionation had been used by Baker and Bennett (*loc. cit.*) without success, and since the purification used by Flint was not unexceptionable, it was thought worth while to repeat the work. By the great kindness of Prof. Marckwald, 200 grms. of telluric acid, which had been re-crystallised many times, were placed at our disposal for the purpose. It was not thought necessary to purify the material further. The acid was boiled with hydrochloric acid until no further odour of chlorine could be observed. The solution of tellurium tetrachloride was evaporated, and dissolved in as small a quantity of hydrochloric acid as possible, the volume of the solution being 150 cc. This was poured by degrees into 3650 cc. of water, which was heated to the boiling-point, the proportion of tellurium tetrachloride to water being the same as that employed by Flint. The precipitated oxide was dissolved in the minimum quantity of hydrochloric acid, and again partly precipitated by boiling water. The process was repeated until four fractionations had been performed. According to Flint, the dioxide last precipitated should contain tellurium with an atomic weight of nearly a whole unit lower than the accepted atomic weight.

In determining the atomic weight, a method was employed which had given very constant results in the hands of one

of us, namely, the conversion of the element into the tetrabromide. To obtain the element, the dioxide was dissolved in hydrochloric acid, and the solution after heating to the boiling-point, was saturated with sulphur dioxide obtained from the liquefied gas. After remaining for a night, the precipitation was complete. The precipitate was washed with boiled distilled water until the washings gave no opalescence with barium chloride. After drying, the tellurium was melted in a current of hydrogen prepared by the electrolysis of purified barium hydroxide solution. The element prepared by this method was obtained in the form of an elongated button showing foliated crystallisation on the upper surface.

The method of determination of the atomic weight was precisely the same as that described in the previous paper. New platinum-plated weights were used, which were carefully standardised. The balance was an Oertling No. 5, which is only used for atomic weight work. All the weights are calculated to vacuum standard. The results of the determinations were:—

	Weight of tellurium.	TeBr ₄ formed.	Atomic weight.
1.	0.87822	2.20103	127.55
2.	0.59706	1.49640	127.55
3.	0.69189	1.73442	127.53
4.	0.62732	1.57254	127.53
5.	0.58307	1.46162	127.53
Mean			127.54

Determinations of the atomic weight of the material similarly purified, but without the attempted fractionation, gave a mean result of 127.53. Since no diminution was found in the atomic weight after four partial precipitations, a treatment which Flint had found to result in a diminution of nearly a whole unit in the atomic weight, we considered it unnecessary to proceed further. It seems possible that the methods of purification used by Flint were insufficient to remove some element of lower equivalent than tellurium, and that this impurity accumulated when the process of fractionation was repeated.

In working up the residues for return to Prof. Marckwald, two more precipitations of the tetrachloride by water were effected. In the last precipitation there was noticed a part of the precipitate which was orange in colour. On separation of this from the mass of white dioxide, it was proved to be tellurium trioxide, both by its giving off oxygen when heated alone, and by the evolution of chlorine on treatment with hydrochloric acid.

In order to see if this formation of trioxide afforded any help towards the explanation of Flint's results, some purified tellurium trioxide was treated with nitric acid, and the solution crystallised. The crystals were dried at 140°, and on decomposition gave a percentage loss of 17.35, the calculated loss for 2TeO₂.HNO₃ being 16.49 (Te = 127.54). It thus appears that some formation of the higher nitrate takes place, and it is just possible that this may be the origin of the low atomic weights found by Flint. The atomic weight of the element, on the assumption that only 2TeO₂.HNO₃ was present, deduced from this last experiment, would be 118.31. The formation of the trioxide, noted above, has been traced to the purified hydrochloric acid. It was inadvertently left exposed to the bright light prevalent during the last few weeks, and it was found to be seriously contaminated with chlorine.

We wish to express our thanks to Prof. Marckwald for the loan of the highly purified telluric acid, and also to Dr. A. Scott for a supply of purified bromine.—*Transactions of the Chemical Society*, 1911, xcix.

THE

DETERMINATION OF MOISTURE IN BUTTER.

By A. C. D. RIVETT, B.A., B.Sc.

CONSIDERABLE attention has been devoted of late years to the problem of the accurate determination of moisture in butter. The most favoured method is by direct vaporisation by heat of the moisture, loss of other constituents being considered negligible. Henzold (*Journ. Chem. Soc.*, 1891, A, lx., 1300) melted the butter on pumice, and then heated for two hours in a water-oven. Bird (*Journ. Am. Chem. Soc.*, 1904, xxvi., 818) made use of a current of hot dry air. Fahion (*Journ. Chem. Soc.*, 1906, A, [2], xc., 402) applied direct heat from a Bunsen flame, the butter being well stirred. The "short test" used in many butter factories is similar. That known as the "long test" consists in heating for an hour in an air-oven at 60° to 105°, for a second hour at 105° to 120°, while for a third the temperature is maintained constant at 120°. In the sequel, this is referred to as the heating method. Other principles have been applied; thus Poda (*Journ. Chem. Soc.*, 1901, A, [2], lxxx., 482) extracted the water by means of sulphuric acid, measuring its amount by the increase in volume of the latter. Aschman and Arend (*Journ. Chem. Soc.*, 1906, A, [2], xc., 814) distilled the water off with xylene, determining the volume of it which separated on cooling. They claim an accuracy within 0.1 per cent. Richmond (*"Dairy Chemistry,"* 1899, p. 252) distils off the water with a little alcohol at 100°.

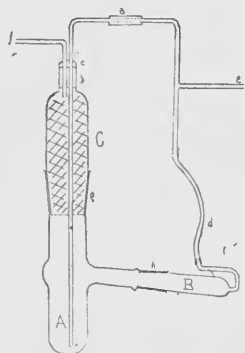
The use of powdered carbide of calcium for estimating moisture in organic and other substances was first described by Danne (*Proc. Soc. Chem. Ind. Victoria*, 1900), and later for estimations in cordite by Dupré (*Analyst*, 1906, xxxi., 213). The principle has been applied in Australia to the estimation of moisture in wool (Orme Masson, *Proc. Soc. Chem. Ind. Victoria*, 1909), and by Cripps and Brown (*Analyst*, 1909, xxxiv., 519) to determinations in spices. More recently, J. I. O. Masson (*Trans. Chem. Soc.*, 1910, xcvi., 851) has proved the carbide method capable of giving in some cases a quantitative measure of water of crystallisation, and in others a quantitative yield of a lower hydrate. The same author (*CHEMICAL NEWS*, 1911, ciii., 37) has suggested directions of extended application of the method, one of them being the object of the present work, viz., the estimation of moisture in butter.

A first attempt aimed at direct measurement over mercury in a nitrometer of the evolved gas. It proved unsatisfactory in that to obtain a moderate volume of gas, say, 40 cc., so small an amount of butter is required that the fairness of sampling becomes open to doubt. An apparatus of larger volume required, too, considerable amounts of mercury, and the necessity of heating the mixture of butter and carbide led to increased errors in reading volumes, unless measurements were made in a thermostat. The use of an anhydrous solvent, suggested by Masson (*loc. cit.*), obviates heating, but it was found that acetylene was evolved too slowly from toluene for the method to be a success. Nor is it satisfactory to absorb the gas in ammoniacal silver nitrate, back titrating the salt remaining unconverted to insoluble silver acetylide (Berthelot, *Comptes Rendus*, 1899, cxxix., 361). Absorption is not sufficiently rapid, nor the evolution of acetylene well enough under control. A high degree of accuracy proved, however, to be attainable by direct determination of the weight of gas evolved when about 10 grms. of butter were heated with carbide. The sketch shows the apparatus adopted to scale $\times$ one-fourth.

It consists of three main parts, A, B, and C, connected by well-ground joints, *g* and *h*. Butter is placed in A, carbide (about 4 to 5 grms.) in B, and C is filled with glass-wool freely sprinkled with the powder. Acetylene is probably soluble in melted butter, hence to ensure its expulsion a stream of gas may be driven along *e a k* and bubbled through the mixture, *d* being clipped. When *d* is open the stream serves to clear all acetylene out of the rest of the

Appointment.—Mr. A. T. Hill, formerly one of the Managers of Messrs. Burroughs, Wellcome, and Co., was appointed Managing Director of Day and Martin, Ltd., on October 2nd last.

apparatus preparatory to weighing. Two towers of caustic potash on pumice, and one of sulphuric acid, serve to purify the gas before it enters *e*. *f* is an exit tube, and during a determination a U-tube containing sulphuric acid on pumice is attached to it. *c* is a layer of sealing-wax over the cork *b*. During weighings rubber caps are fitted to *e* and *f*. In an estimation B is filled with carbide, and the whole apparatus weighed. Butter (about 10 grms.) is introduced into A, and the weight again taken. The U-tube is attached at *e*, rather more than half the carbide tipped into A, and the temperature of the butter raised gradually to the necessary height (see below). Acetylene is evolved, and frothing is readily kept under control by shaking the apparatus. Some water always escapes with the acetylene, and condenses on the upper walls of A, or passes into *c* and acts on the carbide there. Hence it is necessary, when the evolution has nearly ceased, to cool the lower part of A (by immersion in mercury) until the mixture solidifies, and then to shake the rest of the carbide well round the walls of A. The butter and carbide are again raised to the required temperature, and the gas current passed for some time after all evolution of bubbles from the liquid has ceased. Usually about 2 litres were



passed. The apparatus is allowed to cool while the current is still passing, and is then weighed for the third time. The difference between the first two weighings (made to the nearest mgrm.) gives the weight of butter; between the second and third, that of acetylene.

The quantitative relation between water and the gas evolved from carbide does not correspond accurately with the equation—



To determine it, it is convenient to absorb a weighed amount of water in A on sand previously dried at a red heat, and cooled in a desiccator. Table I. gives a number of standardisations, in all of which the mixture of moist sand and carbide was well heated. Nos. 1 and 2 are from the top, 3 and 4 from the bottom of the first tin of carbide used, and 5 from the second tin.

TABLE I.

	1.	2.	3.	4.	5.
Weight of water ..	0.5637	0.7207	0.690	0.7384	0.7778
Weight of acetylene	0.3924	0.5015	0.480	0.5140	0.5410
Weight of acetylene = 1 grm. water ..	0.696	0.696	0.696	0.696	0.696

The theoretical equation requires in the last line 0.722 grm., of which the yield obtained is 96.4 per cent. It is of interest to quote determinations of the volume of gas evolved in the cold by the action of water on the same carbide. Consecutive values obtained were 5.70, 5.735, 5.70, and 5.715 cc. under normal conditions of temperature and pressure, per 10 mgrms. of water. Theory requires 6.18 cc., of which the mean figure 5.71 represents only 92.4 per cent. Such results tend to confirm the suggestion

by Masson (*loc. cit.*) that, besides acetylene, a polymer may be formed, and also that commercial carbide may contain quicklime.

The preliminary experiments, which need not be quoted, have an interest mainly in showing the difficulties in the satisfactory sampling of ordinary butter, even by taking adjacent portions of the same lump. In subsequent work the customary device has been adopted of first melting the butter, forming an emulsion with the water, and stirring till solidification is well advanced. Even samples are readily obtained from such a mixture.

In Table II. are given the figures for a series of duplicate determinations by both the carbide and heating methods. In the latter, aluminium dishes 7 cm. diameter and 5.5 cm. depth were used, and duplicates were given precisely the same three hour treatment between 60° and 120°.

TABLE II.

No.	Percentage (carbide).	Mean.	Percentage (heating).	Mean.	Difference.
1.	10.98 10.93	10.96	10.94 10.99	10.97	0.01
2.	12.18 12.07	12.13	12.25 12.26	12.26	0.13
3.	12.33 12.33	12.33	12.58 12.63	12.61	0.28
4.	13.67 13.74	13.72	14.05 14.09	14.07	0.35
5.	14.23 14.25	14.24	14.66 14.68 14.68 14.69	14.68	0.44
6.	14.82 14.88	14.85	15.06 15.13	15.10	0.25
7.	16.47 16.35	16.41	16.77 16.66	16.72	0.31
8.	19.63 —	19.63	19.96 19.95	19.96	0.33

The differences are all in the same direction, the carbide method giving the lower result. The butter of No. 5 was an unsalted specimen, smelling strongly of butter-milk, and during the heating process it became much browner, evidently therefore suffering more decomposition than any other sample. This may account for the high difference between the methods. The figures indicate that the carbide method may be relied upon to give regular results, and that these come about 0.2 or 0.3 below the percentage figures obtained by the heating method. The differences are less with smaller percentages of moisture, but whether or not they are negligible when the moisture falls below a certain limit, as seems to be indicated in No. 1, requires further testing.

Various suggestions may be made to account for the small differences by the two methods.

1. The gas bubbled through the heated butter was usually air, and oxygen may have been absorbed by unsaturated constituents, thus making the apparent loss of acetylene too low. To test this, air was replaced by hydrogen in one of the determinations of No. 1. The figures are 10.98 (air), 10.93 (hydrogen). In No. 2, nitrogen was substituted, and the result obtained was 12.18, against 12.07 with air. This is a larger difference than is usual, but in No. 4 a percentage of 13.67 was obtained with nitrogen, and 13.74 with air. Hence although absorption of oxygen is *a priori* probable, any error due to it is negligible.

2. The temperature to which the mixture of carbide and butter was heated may have been insufficient for complete action. That temperature is an important point is shown by a comparison of the figures in Table III. with those in Table II. In the former, the butter mixture was heated by a small flame some 9 inches below it, only to so high a temperature that a thermometer in contact with the outside of A registered between 60° and 70° C.

TABLE III.

No.	Percentage (carbide).	Percentage (heating).	Difference.
1.	12.06	12.36	0.30
2.	12.09	12.78	0.69
3.	12.20	13.10	0.90
4.	14.68	15.67	0.99
5.	17.37	18.37	1.00
6.	19.09	20.26	1.17
7.	19.41	20.65	1.24
8.	21.32	22.58	1.26

The results of the second column are very low, pointing to the conclusion that this degree of heating is insufficient to bring moisture and carbide completely into contact. But in the experiments of Table II. the bulb A was heated directly with a Bunsen flame, so that the temperature must have been well up to, if not over, that of the heating method, and any water escaping the carbide action in the bulb A would have been driven off and acted upon in C, or on the walls of A.

3. In the heating method some other constituent of the butter or decomposition product (which, in the carbide apparatus, is condensed partly at least in C) may be expelled along with the water. Quantitative evidence is not readily obtained, but the qualitative evidence is decisive. The smell noticed during the heating process, the discoloration, sometimes slight, sometimes very marked (a variation suggesting unreliability for purposes of comparison of different kinds of butter), and the change in physical properties at the end of the heating, suggest more alteration than might reasonably be expected to follow a mere expulsion of water. Further, on distilling water from butter the distillate is not pure. Thus in one experiment 200 cc. of water were distilled from 85 grms. of butter, a bulb column being used to avoid splashing. The bulk came over within 2° or 3° of the boiling-point of pure water, was slightly cloudy, and possessed a strong unpleasant smell. Later distillates were more cloudy, and formed slight precipitates and surface scums on standing. Small drops could be seen on the surface of the distillate, passing over at 104–106°. If steam under these conditions carries fats over, even in very small quantity, it is reasonable to suppose that the same thing may occur during the heating process.

4. Errors may be introduced in the heating method according as the temperature is raised slowly or rapidly. These, however, appear to be very slight. Thus, a sample of a certain butter was slowly heated during nearly three hours from 50° to 120°. After ten minutes at that temperature it had lost 17.58 per cent of moisture, and the figure was unaltered after a further half-hour at the same temperature. A second sample was introduced at once to a temperature of 110°, and raised in twenty-five minutes to 120°. After an hour at that, the percentage given was 17.57, unchanged after one and a-half hours further at 112°. Other experiments confirmed this, but showed that if the temperature rose much above 120° the results were a good deal increased, e.g., from 10.78 to 10.99 after a short exposure to 160°. As long as 120° is not exceeded, the precise rate of raising the temperature is of slight importance.

It would seem, then, that the small excess of moisture shown by the heating as compared with the carbide method is due to loss of volatile matter expelled with the water vapour. In this connection some figures (kindly communicated by Dr. A. C. H. Rothera) by the method of heating butter to 100° with a little alcohol, may be compared with results by the carbide method. With one butter the alcohol method gave 14.24 and 14.27 per cent. the carbide 14.23 and 14.25 (No. 5, Table II.). With a second, the results were 13.35 and 13.36, and 13.45 and 13.47 respectively. The differences are less than between the carbide and ordinary heating methods.

It would seem probable that in ordinary commercial analysis of butter, errors due to the difficulty of fair sampling may exceed the inherent errors of any method ;

hence it is idle to recommend the carbide method as a substitute for the simpler, though longer, analysis by heating. The usefulness of the former may rather be as a means of standardising more simple, if less accurate, methods.

Summary.

1. A new and accurate method of estimating moisture in butter has been described, depending on the action of the moisture on calcium carbide.

2. The results obtained by it show differences of 0.2 or 0.3, as compared with the percentages given by the ordinary heating method, at least when the butter carries more than 12 per cent of moisture.

3. Evidence is adduced that these small differences are due to loss of other volatile matter than water under the conditions of the heating method.

University of Melbourne.

A RECORD YEAR AT THE ROYAL MINT.

SUCCESS FOR A MANCHESTER FIRM.—GAS CONQUERS COKE.—A SAVING TO THE NATION.

The Annual Report of the Royal Mint, 1910, which has just been published, gives an account of the enormous operations of this Department during the past year. No less than 371 tons of gold were melted during the twelve months, this amount being more than double the average of the ten years, 1899–1908.

A large quantity of nickel is melted at the Mint for coinage for East and West Africa. The quantity of gold, silver, bronze, and nickel melted during the year amounted to the prodigious total of 1251 tons, and even then the demand for coinage was so great that 250 tons of bronze blanks had to be purchased from contractors. The total number of coins struck during the year was 158,204,241, the value of these amounting to £28,040,217, which is the highest record for the Royal Mint.

Some very important changes have been made in the methods of melting the various metals used for coinage. Preliminary experiments on the use of gas and oil instead of coke have been in progress since early in 1909, and these experiments have involved the preparation of many designs for furnaces of various sizes, and the testing of a number of burners for obtaining high temperatures, some specially designed, and others of patterns already in use in various trades. Electric furnaces were also experimented with.

In connection with these experiments a number of visits were made to factories both in London and the provinces, where oil or gas were used for melting purposes, and the Superintendent was directed in January, 1910, to visit the United States and Canada, where oil is largely used, in order to collect data which were likely to be of assistance in arriving at a decision.

Oil furnaces, burning both petroleum and creosote oils, were tested under very varying conditions, and with air at pressures varying from 2 lbs. to 25 lbs., but it was finally decided that liquid fuel was unsuitable.

In the experiments with ordinary town's gas a variety of systems was tested, involving the use of gas at ordinary and high pressures, combined with variations in the pressure of the air, and the burner ultimately adopted was made by Mr. S. N. Brayshaw, of Manchester.

For the Brayshaw burners in use at the Mint the gas is taken at the ordinary pressure in the main (about 3 in. of water), and mixed with air from a powerful blowing engine at about 2 lbs. pressure. With care the noise of these burners can be reduced sufficiently to be unobjectionable, the furnace linings compare very favourably with those hitherto used for coke in regard to endurance, and the crucibles used for gold are found to last longer (each crucible serving for an average of eighteen heats as against twelve when coke is used).

The adoption of gas as a fuel in place of coke has been accompanied by several incidental economies, and it is interesting to note that the present charge for fuel averages about 4½d. per cwt. of standard gold bullion as against 7d. when coke was used. It should be added that in this statement the fuel needed to warm up the furnace in the morning has been eliminated, but, including this, the cost rarely exceeds 5d. per cwt. on a day's work.

During 1910 the Mint installed sixteen gas heated furnaces, each capable of taking a 400 lb. crucible, and fired with Brayshaw gas burners. These sixteen furnaces have a maximum capacity of 2½ tons of sterling silver, or 2½ tons of bronze per melt, and four melts of silver, or three of bronze, can be made in an ordinary working day (8 a.m. to 6 p.m.). Also five furnaces similarly gas heated, but of a smaller size, are in use for melting gold.

Considering the large quantity of metal melted at the Mint, it will be seen that a very substantial saving in the cost of fuel alone has been effected for the nation by the use of gas. The incidental economies are, however, still greater. The cost of carting and handling both coke and clinker is saved, and the room formerly required for the storage of them is set free. The expenditure on crucibles, which is a large item, has been reduced by 33 per cent. The work of melting is less laborious, the loss of metal is much reduced, and the bars cast are better and more uniform.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 16th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Discovery of a Novel Type of Flint Implements below the Base of the Red Crag of Suffolk, &c." By Sir E. RAY LANKESTER, F.R.S.

1. Flint implements of human manufacture have been discovered by Mr. J. Reid Moir, of Ipswich, in the detritus-beds at the base of the Red Crag in Suffolk and by Mr. W. G. Clarke at the base of the Norwich Crag in Norfolk.

2. These implements are of a novel type—the "rostricariate" or "eagle's beak"—but include also scrapers, hammers, and large one-sided picks. They do not include any forms resembling the Chellian and Acheulian ovate implements. The Sub-crag type (rostricariate) is essentially compressed from side to side. The Chellian and Acheulian and Moustierian types are essentially depressed or flattened like a leaf.

3. They were manufactured at a period previous to one of severe glaciation, which set in before the lowest beds of the Red Crag and Norwich Crag were deposited, and characterise a phase of human development earlier than any hitherto known by equally indisputable evidence.

4. The rostricariate implements were not improbably used for dressing and smoothing the skins of animals.

5. On the land surface from parts of which these implements were moved into the detritus-beds at the base of the East Anglian "Craggs," similar implements remained, which were embedded in the subsequent deposits of the glacial period and have been found in a few isolated instances in Mid-glacial sands and Boulder Clay.

6. The Red Crag is commonly regarded as of greater geologic age than its proper fauna would indicate. Its mammalian fossils are derivatives of an earlier age, and the few molluscs of Pliocene character found in its earlier layers are lingering survivors from a warmer condition of the sea. They became extinct at the early onset of the

conditions proper to the Red Crag sea. The Red Crag should be grouped with the Pleistocene rather than with the Pliocene series.

7. The race of men who manufactured the Sub-crag flint implements probably lived on the land surface not remote from the sea, during the period of the Coralline Crag, which was characterised by a warmer climate than that of the Red Crag and may justly be regarded as marking the close of Pliocene conditions in this part of Europe. The land barrier joining Britain to Scandinavia, which had kept the southern part of what is now the North Sea from access of cold northern waters ever since the earliest Tertiary period, disappeared at the beginning of the deposition of the Red Crag.

8. If these propositions are justified, it remains a question for later enquiry whether the men who made the Sub-crag implements were of greater antiquity than those who made the implements (so-called Eoliths) of the high Plateau-gravels of Kent, or than those recognised by some archaeologists as makers of roughly chipped flints found in other localities but not hitherto generally admitted as of human workmanship.

9. In any case the implements from the Sub-crag beds in East Anglia are of special and very distinct type and can not be associated with any known from any other locality.

"Studies in Heredity. I. The Effects of Crossing the Sea-urchins Echinus esculentus and Echinocardium cordatum." By Prof. E. W. MACBRIDE, F.R.S.

"Influence of Ionised Air on Bacteria." By Prof. W. M. THORNTON.

"Intrinsic Factors in the Act of Progression in the Mammal." By Dr. T. GRAHAM BROWN.

"Refractive Indices of the Eye Media of some Australian Animals." By Dr. J. L. JONA.

"Permeability of the Yeast Cell." By S. G. PAINE.

"Ventilation of the Lung in Chloroform Narcosis." By G. A. BUCKMASTER and J. A. GARDNER.

The authors give a number of plethysmographic tracings to show the lung-ventilation during chloroform anaesthesia with different percentages of chloroform and ether, and also analyses of the blood gases.

They show that with unimpeded respiration under anaesthesia by chloroform given at a slight positive pressure the ventilation of the lung takes place at a lowered level. During a narcosis in which respiration continues the lung-ventilation is diminished in the first three minutes by about 60 per cent of its original value, and by a similar amount after prolonged anaesthesia.

They consider that the carbon-dioxide content of the blood is reduced below a threshold value by any state of hyperpnoea prior to administration of the drug, and this diminution in carbon-dioxide content plus the diminished excitability of the respiratory centre would suffice to slow or abolish the activity of the centre.

Gas analyses actually show that with a deep and rapid respiration there is a marked fall in the carbon-dioxide content of the blood.

They also bring forward evidence to show that the diminution in oxygen content of the blood during chloroform narcosis is not due entirely to diminished alveolar ventilation, but to the action of the drug on the red corpuscles.

"(i.) On the Boiling-point of Water"; and (ii.) "On the Boiling-points of some Saturated Aqueous Solutions." By LORD BERKELEY, F.R.S., and M. P. APPELBY.

"Heating Effect of the Currents in Precise Measurements of Electrical Resistance." By Dr. R. T. GLAZEBROOK, F.R.S., W. R. BOUSFIELD, and F. E. SMITH.

CHEMICAL SOCIETY.

Ordinary Meeting, October 19th, 1911.

Prof. PERCY F. FRANKLAND, LL.D, F.R.S., President, in the Chair.

(Concluded from p. 254).

253. "The Action of Chlorine on Alkalis and of Carbon Dioxide on Bleaching Powder." By ROBERT LLEWELLYN TAYLOR.

In reply to Higgins' suggestion (*Trans.*, 1911, xcix., 858) that the increased bleaching efficiency of a solution of bleaching powder on the removal of free lime or the addition of chlorides (Taylor, *Trans.*, 1910, xcvi., 2541) is not due to the reversal of the action and consequent liberation of chlorine, but, in the first case, to the further action of the carbon dioxide of the air, and, in the second case, to the increased attraction of such solutions for the carbon dioxide of the air, the author pointed out that most of his experiments were performed either in absence of air or with air from which the carbon dioxide had been removed, and described further experiments performed in closed vessels, in which he obtained similar results.

Higgins further stated that other neutral salts of sodium had a similar stimulating effect on the bleaching action of a solution of sodium hypochlorite to the chloride.

Further experiments by the author show that if a solution of sodium hypochlorite contains considerable excess of free alkali, its bleaching action is very slow, and it is not much stimulated by the addition of any sodium salts, but if there is not much free alkali present the stimulating action of sodium chloride is much greater than that of other neutral sodium salts.

The author further pointed out that Higgins' suggested explanation of the action of carbon dioxide on bleaching powder is not really very different from his own. Higgins represents the action by two equations, and the author by three, the second and third of the latter being merely a simplification of Higgins' second.

254. "The Relation between Residual Affinity and Chemical Constitution. Part II. Certain Compounds of Nitrogen." By HANS THACHER CLARKE.

An account was given of a study of the reactivity towards alcoholic benzyl chloride under standard conditions, and the refractive power of a series of open-chain and cyclic tertiary amines containing one and two nitrogen atoms in the molecule. The conclusion was put forward that derivatives of piperazine display abnormal reactivity and refractive power when compared with the corresponding open-chain compounds. In a series of derivatives of piperidine, it was shown that the reactivity increased similarly when the nitrogen atoms were present in the 1:5-position in a normal chain.

255. "Theory of Dyeing: Colour and Molecular State of Picric Acid." By WILLIAM PORTER DREAPER.

Picric acid in the anhydrous state is probably colourless. In the presence of moisture it is yellow, and possibly then has a quinonoid structure. In continuation of a previous investigation into the relative inhibiting action of fibre colloids on this colour change (Dreaper and Stokes, *Journ. Soc. Dyers*, 1909, xxv., 10), the action of toluene on picric acid when present within the fibre area has been examined.

The experimental results indicate that even in the case of cotton, although the change to the colourless type takes place readily in the presence of dehydrating agents, yet the presence of toluene will not bring about this change, in spite of the known fact that picric acid has little affinity for vegetable fibres in the presence of water; also, that under certain conditions picric acid in the yellow state will be adsorbed by cotton from a colourless toluene solution.

256. "Electromotive Forces in Alcohol. Part II. The Hydrogen Electrode in Alcohol and the Influence of Water on its Electromotive Force." By ROBERT TAYLOR HARDMAN and ARTHUR LAPWORTH.

Concentration cells reversible to hydrogen ions with solutions of hydrogen chloride in absolute alcohol gave potentials which were constant and reproducible within a fraction of a millivolt. Results with solutions not weaker than N/20 were in fairly good agreement with those calculated by employing the transport numbers deduced in Part I. (*Trans.*, 1911, xcix., 1420; with lower concentrations, discrepancies of several millivolts were found.

Water depresses the potential of the hydrogen electrode in alcoholic hydrogen chloride, and when the acid is dilute the results indicate a fall in the concentration of the "free" hydrogen ions which is very close to that anticipated on the assumption that the availability of the acid is a measure of this concentration as well as of the catalytic activity of the cations of the acid in a given solvent (*Trans.*, 1908, xciii., 2168, 2190 *et seq.*; 1910, xcvi., 23).

With N/100-hydrochloric acid in both compartments of such a concentration cell, the potentials observed when water is added to one compartment indicated a "water value" for absolute alcohol = 0.132 at 25°; with N/500-hydrochloric acid and N/10-lithium chloride to minimise potential differences at the liquid boundary, the "water value" indicated was 0.122 at 25°. These numbers are intermediate between those previously deduced from (i.) measurements of the catalytic and (ii.) the salt-forming activity of hydrogen chloride in absolute alcohol by Goldschmidt and Udby (0.15) and by Lapworth and Partington (0.10) respectively.

257. "Notes on New Coumarin Derivatives." By ARTHUR CLAYTON.

In view of the characteristic odour of the 5-nitro-substituted coumarins (Clayton, *Trans.*, 1910, xcvi., 1388), the author attempted to prepare 5-nitrocoumarin, since its odour might reasonably be supposed to be stronger than that of the foregoing compounds.

A study of the action of nitric acid on the homologues of coumarin indicated a tendency for the nitro-group to enter position 5 when position 6 is already occupied by a substituent, whence it was hoped that 6-aminocoumarin would yield 5-nitro-6-aminocoumarin when nitrated, and that the amino-group could be subsequently removed by the diazo-reaction.

Preliminary experiments showed that 6-aminocoumarin yielded an unworkable tar when treated with nitric acid, either alone or in solution in acetic or sulphuric acid, but 6-acetylaminocoumarin, when dissolved in nitric acid (D 1.5) cooled to 10°, yielded a solution which, on dilution with water, furnished an abundant and almost white solid. The nitro-6-acetylaminocoumarin so obtained crystallised from glacial acetic acid in pale yellow needles, melting at 222–223°:—

0.1452 gave 0.2828 CO₂ and 0.0590 H₂O. C = 53.10; H = 4.52.

0.1438 gave 15.1 cc. N₂ at 21° and 742 mm. N = 11.67. C₁₁H₈O₅N₂ requires C = 53.23; H = 3.23; N = 11.29 per cent.

Nitro-6-acetylaminocoumarin proved to be easily hydrolysed by boiling with sulphuric acid diluted with three times its volume of water for thirty minutes. The product, nitro-6-aminocoumarin, was obtained by further dilution with water, and was then crystallised from glacial acetic acid, when orange needles, melting at 238–240°, were obtained:—

0.1182 gave 0.2266 CO₂ and 0.0354 H₂O. C = 52.31; H = 3.36.

0.1432 gave 17.5 cc. N₂ at 21° and 742 mm. N = 13.58. C₉H₆O₄N₂ requires C = 52.43; H = 2.91; N = 13.59 per cent.

All attempts to eliminate the amino-group from the foregoing compound proved unsuccessful, owing to the extreme ease with which coumarin-6-diazo-5-oxide is formed. The latter compound is produced in greatest quantity when nitro-6-aminocoumarin (1 grm.) is mixed with absolute alcohol (10 cc.), and concentrated sulphuri

acid (4 to 6 drops) and an excess of amyl nitrite are consecutively added. On warming, the mixture becomes less pasty, and then, rather suddenly, a mass of crystals is deposited. This product was separated and crystallised from very dilute alcohol, when yellow needles were obtained, melting with abrupt decomposition at 155–160°. It yields no definite product when boiled with acids or alkalis:—

0.1468 gave 0.3076 CO₂ and 0.0307 H₂O. C=57.14; H=2.32.

0.1203 gave 15.0 cc. N₂ at 18° and 770 mm. N=14.60. C₉H₄O₃N₂ requires C=57.45; H=2.13; N=14.89 per cent.

During experiments performed in other directions with the hope of obtaining odorous nitrocoumarins, the following compounds were also obtained.

6-Methylcoumarin was prepared by heating together 2-hydroxy-*m*-tolualdehyde (3 grms.), anhydrous sodium acetate (3 grms.), and acetic anhydride (5 grms.) in an oil-bath at 180° for four hours. The product solidified to a brown cake on cooling. This was boiled with water to remove the sodium acetate, and the residue from the cold liquid ground up with methyl alcohol (2 to 3 cc.). The filtered product was then crystallised, first from dilute methyl alcohol and then from petroleum, after which it formed white needles, melting at 75°. These crystals are somewhat soluble in water, and possess an odour of coumarin:—

0.1083 gave 0.2983 CO₂ and 0.0520 H₂O. C=75.11; H=5.34.

C₁₀H₈O₂ requires C=75.00; H=5.00 per cent.

Nitro-6-methylcoumarin was obtained by dissolving 6-methylcoumarin in concentrated sulphuric acid (20 parts), and adding nitric acid (1 molecule). After twenty minutes, the liquid was poured on ice, and the precipitated solid crystallised from alcohol, when white inodorous needles, melting at 147–148°, separated:—

0.1576 gave 9.6 cc. N₂ at 23° and 766 mm. N=6.92.

C₁₀H₇O₃N requires N=6.83 per cent.

4:8-Dimethyl-6-tert.-butylcoumarin. — This compound resulted from the condensation of equimolecular quantities of *p*-tert.-butyl-*o*-cresol and ethyl acetoacetate in the presence of concentrated sulphuric acid. White inodorous needles were obtained, melting at 159–160°:—

0.1980 gave 0.5664 CO₂ and 0.1422 H₂O. C=78.03; H=7.98.

C₁₅H₁₈O₂ requires C=78.26; H=7.83 per cent.

The substance appears to behave abnormally toward nitric acid, owing probably to the presence of the tert.-butyl group. The nitration product forms white needles, melting at 240–241°, and possesses a pleasant but not very marked odour.

258. "The Temperature-coefficient of the Electrical Conductivity of Hydrogen Chloride in Alcoholic Solution." By JAMES RIDDICK PARTINGTON.

The experiments proposed in a former communication (Lapworth and Partington, *Trans.*, 1911, xcix., 1426) are now completed, and the conductivities of alcoholic hydrogen chloride at 0°, 18°, and 25° have been determined.

The values at infinite dilution are found to be:—

λ_{∞} at 0° = 46.50,

λ_{∞} at 18° = 60.00,

λ_{∞} at 25° = 66.50.

From these the mean value of the temperature-coefficient, α_{∞} , is found to be 0.0178 units of λ_{∞} at 0° per 1°, and is therefore normal.

259. "The Constituents of the Oil of *Pinus longifolia*." By HENRY HALIBURTON ROBINSON.

By fractional distillation, the oil of *Pinus longifolia* was found to be divisible into two portions; one portion, amounting to about one-third of the whole, was of a much

lower boiling-point than the other, and was found to be *l*-pinene. The remaining two-thirds was mainly composed of an oil boiling at 173°, having D_{15/15} 0.867 and n_D about +13°. From this, by treatment with dry hydrogen chloride, sylvestrene dihydrochloride was obtained, from which sylvestrene was regenerated. From the mother-liquors left after removing as far as possible the sylvestrene dihydrochloride, dipentene was obtained. It is thought very possible that the sylvestrene is not present as such in the original oil, but that a terpene is there contained, which unites with hydrogen chloride to form sylvestrene dihydrochloride, just as pinene yields a hydrochloride from which camphene is obtained when the hydrogen chloride is removed.

260. "The Active Constituents of the Indian Solanaceous Plants; *Datura Stramonium*, *D. fastuosa*, and *D. Metel*." By ALBERT EDWARD ANDREWS.

It was found that in the Indian *Datura Stramonium* plants the percentage of total alkaloid in the stems was 0.25; in the leaves, 0.41 to 0.45; and in the fruits, 0.46 per cent; with one exception this alkaloid consisted of hyoscyamine either alone or associated with a small proportion of scopolamine. The results indicate that the Indian plant bears favourable comparison with the European and Egyptian plants as regards the amount of total alkaloid, but the presence of scopolamine in some of the Indian samples appears to be a point of difference.

In the Indian *Datura fastuosa* samples, the total alkaloid varied from 0.1 in the roots to 0.2 in the fruits, and scopolamine was found to be the predominant alkaloid. In these respects the Indian plant closely resembles the European plant.

In the Indian *Datura Metel* samples the seeds and the leaves contained 0.25, and the capsules 0.12 per cent, of total alkaloid. On comparing the results with those recorded for the European species it appears that in the Indian plant the amount of total alkaloid in the seeds and in the leaves is only about one-half what it is in the European plant, but with one exception the samples resemble the latter in so far that scopolamine is almost unaccompanied by other mydriatic alkaloids.

261. "Contributions to the Chemistry of the Terpenes. Part X. The Action of Chromyl Chloride, Nitrous Acid, and Nitric Acid on Bornylene." By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

On treatment with chromyl chloride dissolved in carbon disulphide, bornylene is converted into a solid additive product, C₁₀H₁₆.2CrO₂Cl₂, which is decomposed by water, giving a chloroketone, C₁₀H₁₅OC₂H₅, and an aldehyde, C₉H₁₅.CHO. The ketone, a crystalline solid, m. p. 165°, gives a semicarbazone, melting at 234–235°, and yields camphoric acid when oxidised with potassium permanganate, and camphor when heated with alcoholic potassium hydroxide under pressure. It therefore appears to be a new chlorocamphor. The aldehyde was proved to be camphenilanaldehyde, a derivative of camphene, which has been prepared in several different ways from that hydrocarbon. The direct formation of this camphene derivative from bornylene indicates close similarity in the molecular structure of these terpenes.

It has been observed that camphenilanic acid, C₉H₁₅.CO₂H, can be converted into isocamphenilanic acid by repeated crystallisation from water, alcohol, or light petroleum, and also that the semicarbazones obtained from camphenilanaldehyde and isocamphenilanaldehyde respectively are identical, and that each yields the isocamphenilanaldehyde when decomposed with dilute acids.

Bromo-isocamphenilanic acid, a crystalline solid, m. p. 204–205°, was prepared by converting isocamphenilanic acid into its chloride, C₉H₁₅.COCl, a dense liquid, b. p. 118°/25 mm., heating this with bromine under pressure, and decomposing the chloride of the bromo-acid, C₉H₁₄Br.COCl, which is also a heavy viscous liquid, with water. When warmed with aqueous sodium carbonate, the bromo-acid does not give a corresponding hydroxy-

acid, but is converted into an unsaturated acid, $C_9H_{13}CO_2H$, a colourless crystalline solid, m. p. 147° .

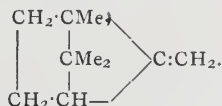
Bornylene shows a general resemblance to camphene in its behaviour towards nitrous acid, but different products are obtained on attacking these terpenes with nitric acid.

On treatment with nitrous acid, bornylene yields (1) a nitrosite, $(C_{10}H_{16}N_2O_3)_2$, which crystallises in silky needles, m. p. 163° , and yields camphoric acid on oxidation; (2) an oily green liquid, which decomposes when heated, dissolves in solutions of alkalis, and is probably an *isonitrosite*; (3) some camphorquinone; and (4) a very small quantity of a colourless crystalline compound, m. p. $84-85^\circ$, which is possibly a nitrite.

When heated with nitric acid, bornylene is, for the most part, oxidised to camphoric acid, but some of it is converted into a yellow crystalline compound, m. p. 137° , which has the formula $C_{10}H_{16}(NO_2)_2$, and appears to be *dinitrocamphene*. On reduction with alcoholic ammonium sulphide, this substance yields a compound which crystallises in yellow needles, m. p. $196-198^\circ$, and which apparently is not an amino-derivative. A trace of a colourless crystalline compound, m. p. about 174° , was also found among the oxidation products.

262. "The Constitution of Camphene." By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

Arguments were adduced in support of the view that the constitution of camphene is best represented by the formula:—



263. "Candelilla Wax." By JAMES MCCONNELL SANDERS.

A sample of Candelilla wax, prepared in the month of January from plants collected in Coahuila, had the appearance of a greenish white mass with a granular fracture. It contained a considerable proportion of water, and when freed from this, was dark brown, and gave the following values:—

Melting-point	67.5°
Density	0.9850
Acid value	14.39
Saponification value.. ..	46.76
Iodine value (Hübl).. ..	16.60 per cent
Unsaponifiable matter ..	77.00 "
Hydrocarbons	48.60 "

The wax contained hentriacontane and myricyl alcohol.

264. "A Convenient Method for Determining the Density of Heavy Petroleum." By JAMES MCCONNELL SANDERS.

Heavy crude petroleum and derived products of similar character, such as the more viscous lubricants, "black oils," &c., present difficulties in manipulation when the determination of their density at the standard temperature is attempted by the usual procedure. In the absence of a knowledge of the coefficient of expansion of a particular sample, it is always desirable to determine the density at a temperature as close to the normal air temperature as possible, this being the more desirable when the data to be obtained are subsequently to be utilised for calculation with large volumes of the commercial article.

Crude petroleum are often so dense and viscous that a determination of the density with the pyknometer is very troublesome, and a very appreciable error is introduced by the presence of suspended water, which cannot be removed easily without employing means which are liable materially to modify the density of the oil.

Filtering through hot anhydrous sodium sulphate, or dry salt, usually results in the loss of the more volatile components of the oil, and the use of the filter-pump to facilitate filtration in the cold often gives rise to the same source of error. With increasing density and viscosity of an oil,

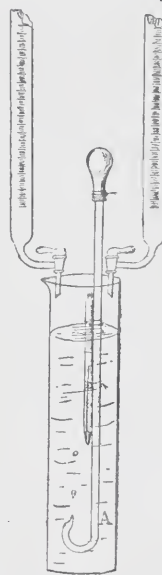
there is increased difficulty of manipulation and simultaneously increased error from included water.

In the simple method about to be described, the error from suspended water is considerably decreased, although not entirely removed; at the same time, the method possesses the advantage of rapidity and economy in the amount of sample employed.

The necessary apparatus consists of a curved glass tube of the form shown, provided with a small rubber bulb or a rubber tube with a pinchcock, according to the density of the oil to be examined. In addition, two graduated burettes of 100 cc. capacity, a cylinder capable of containing 100 cc., a thermometer, and a rubber-tipped glass rod.

Two solutions of alcohol and water are required, one containing 0.5 per cent of alcohol, the other 75 per cent, both by volume. These solutions should be prepared beforehand, and preserved in stoppered stock bottles. The alcohol used should be pure, and the water free from air.

The following method of procedure is to be followed. A well-mixed and representative sample of the oil is poured into the curved glass tube so as nearly to fill it; if the oil



is very viscous the small rubber pear-shaped cap is used to close the upper orifice of the tube, otherwise the tube and pinchcock are employed.

The burettes are then filled each with one of the alcoholic mixtures, the level of the liquids being brought to the zero-point on the burettes, and these are then supported one on each side of the glass cylinder.

The thermometer is then fastened to the filled glass tube in such a manner that its bulb will occupy the central zone of the cylinder when the tube is placed within it so as to rest on the bottom.

About 75 cc. of the more dilute alcohol are then run into the cylinder from the burette, and the glass tube is immersed in the cylinder. By means of the pinchcock or rubber bulb, a single small drop of the oil is expelled from the lower orifice of the tube, when, if the density of the liquid is greater than that of the oil drop, it will immediately rise to the surface, and can be "fished out" by touching it with the rubber-tipped glass rod. A little of the stronger alcohol is then run in from the other burette, and another trial drop of oil expelled; these operations are repeated until the trial drops begin to rise more slowly and assume a spherical form, showing that the density of the alcohol mixture is approaching that of the oil. When

this point is reached, the oil drops should be allowed to exude more slowly, so as to allow any suspended water to be dissolved out by the alcohol, and also to allow the temperature of the alcoholic mixture to coincide with that of the oil in the tube. With a little practice it is possible to procure a number of oil drops floating in various zones of the alcoholic mixture, when the latter should be well stirred, using the tube and attached thermometer for the purpose. As soon as the densities of the mixture and the oil drops are identical, the volumes of the two alcohols used to form the mixture are read off from the burettes, and the density of the mixture is calculated from the amounts used.

Instead of calculating the density of the mixture (which assumes a previous determination of the density of each dilute alcohol), the mixture may be filtered quickly through moistened cotton-wool to separate the oil drops, and the density taken with the hydrometer or the Westphal balance.

A convenient practice consists in preserving the alcoholic mixtures obtained in a series of experiments in closely stoppered bottles, labelled with the corresponding densities and temperatures. These empirical solutions can then be used for approximate determinations of fresh samples of oil.

(We are indebted to the Chemical Society for permission to reproduce the accompanying illustration).

265. "The Probable Cause of the Elimination of a Carboethoxyl Group as Ethyl Carbonate by the Action of Sodium Ethoxide." By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

The cause of the elimination of a carbethoxy-group during the passage of an open-chain nitrile carboxylic ester into a five-ring imino-compound is not due to any condition of strain consequent on the presence of more than one carbethoxy group on any one carbon atom of the ring, but must be ascribed to a tendency which exists for the compound to acquire the hydrogen atom necessary to enable it to react in its tautomeric form.

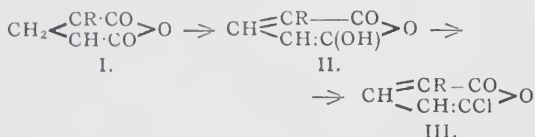
266. "The Chemistry of the Glutaconic Acids. Part II. The Reactions of the Alkylglutaconic Acids having one Mobile Hydrogen Atom." By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

The experiments which have been carried out lead to the following conclusions;—

1. The α -monosubstituted derivatives of glutaconic acid are stable in their *trans*-forms, but can be isolated as unstable *cis*-modifications.

2. The stability of the *cis*-modifications increases with the weight of the group occupying the α -position.

3. The tendency for the mobile hydrogen atom to pass outside the three carbon system is manifested as soon as ring formation is produced from the *cis*-modification. Thus, the normal anhydride (I.) is converted into the hydroxy-anhydride (II.) on distillation, and this is transformed into the chloro-anhydride (III.) by acetyl chloride;—



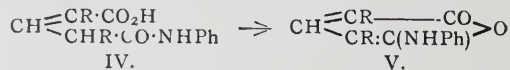
4. The anilic acids of the *cis*-modifications pass into the anilic acids of the *trans*-forms when heated.

5. The di- and tri-substituted derivatives are stable as their *cis*-forms, and cannot be isolated as *trans*-modifications.

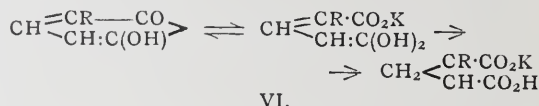
6. The tendency for the mobile hydrogen atom to pass outside the three-carbon system diminishes with the increase of alkyl groups in the molecule.

7. The presence of the mobile hydrogen is indicated, not only by the formation of hydroxy-anhydrides and

chloro-anhydrides, but also by the behaviour of the anilic acids (IV.), which are converted into anilino-lactones (V.) when heated:—



8. The stability of the form which has the hydrogen atom outside the three-carbon system is shown by the fact that the more stable hydroxy-anhydrides behave on titration as monobasic acids, and can be recovered from the solution on acidifying. Analysis of the salts shows them to possess the constitution (VI.). It is only when the neutral solution is warmed that the hydrogen passes back into the three-carbon system, yielding the alkali salt of the *cis*-modification:—



FARADAY SOCIETY.

Ordinary Meeting, November 8th, 1911.

Mr. JAMES SWINBURNE, F.R.S. Past-President,
in the Chair.

AN Address was given to the Society by Dr. EDWARD E. ACHESON, of Niagara Falls.

Dr. Acheson's Address, which was of an informal character, dealt with his own researches on electric furnace products. These researches date back to 1891, when he first made carborundum experimentally by passing a high current by means of carbon electrodes through a mixture of clay and coke in an iron bowl. In spite of the remarkable hardness of the product, it took some time before it found a commercial outlet. The next step was to raise the temperature of the furnace so high that all the silicon was driven off and pure graphite left behind. Eventually a cheap waste Californian ash was used as raw material, and this yielded a non-coalescent, easily pulverised graphite. Last year 13,000,000 lbs. of graphite were sold.

The reduction of silicon from a close mixture of fine silica and fine graphite—the latter envelopes the particles of silica, rendering them conductive—was next attempted and successfully accomplished; it is now made in thousands of tons. Aluminium has also been reduced from a mixture of bauxite and graphite.

From the soft graphite are made the mixtures known as "aquadag" and "oidag." These consist of the graphite in a deflocculated or colloidal form, held in suspension in water and oil respectively. To deflocculate the graphite it is ground in some organic compound, usually gallo-tannic acid containing a little ammonia. The subject of deflocculation was discussed generally. Any non-metallic substance that is amorphous, insoluble, and not fusible can be deflocculated, and the agents may be tannin, extract of straw, or grass, or dung, or any similar body. CO₂ will deflocculate, and the author suggests that perhaps carbon is sometimes fixed in this way in nature. The agent always becomes intimately attached to the graphite during the process, and possibly penetrates its particles, throwing off groups of molecules, or even molecules each of which is surrounded by a minute film of colloidal jelly.

The principal application of deflocculated graphite—suspended in water or kerosine—is as a lubricator. As such there must soon be a great demand for it, for only a fifty years' limit has been assigned to present supplies of natural petroleum. On account of its low viscosity it is greatly superior to heavy oil lubricants, in which heavy frictional losses of power take place. In the fine colloidal state the graphite cannot be squeezed out from between the bearing

surfaces, but it enters the pores and "evens up" the metals, and eventually a surface like glass is produced. The best proportion of graphite to use is about 1 cubic inch in 5 gallons of water. It is noteworthy that steel will not rust in "aquadag," but remains quite bright. The material is in use in all the transport power houses in New York.

The lecture was accompanied by a great many experiments illustrating the production and properties of colloidal graphite.

Dr. J. A. HARKER gave voice to the appreciation of the meeting at hearing Dr. Acheson, to whom all electro-metallurgists were so indebted, and listening to his inspiring and suggestive Address. He remarked that carborundum belonged to a special class of conductors whose conductivity increased at high temperatures.

Mr. L. GASTER hoped that the use of substances such as siloxicon for lining crucibles would develop.

Mr. ROBERT MOND remarked on the immense services rendered to those who were engaged in the development of electrolytic processes by the large graphite electrodes which were the outcome of Dr. Acheson's researches.

Mr. A. HIORTH described the use of colloidal graphite in guns and rifles. When it was not used the barrels eventually burnt out, so that its use enormously enhanced the life of the guns, besides increasing the range by 15 per cent. Graphite, however, was expensive in Europe, and he hoped that it would be made in Norway.

Mr. RITCHIE described his experiences with carborundum wheels. He hoped engineers would become acquainted with the new graphite products.

Dr. H. BORNS, referring to Mr. Hiorth's remarks, said that the use of graphite probably prevented a discharge of powder in front of the bullet, which was known to take place in the ordinary way.

Dr. ACHESON replied in detail to the points raised. Graphite was very popular in the States for gun lubrication. About 4 grains were required for each bullet, and there was practically no wear of the rifle at all. The cost of graphite would probably be reduced in the near future, but the consumption as yet did not justify its being made at more than one centre.

CORRESPONDENCE.

PURIFYING MERCURY IN THE LABORATORY.

To the Editor of the Chemical News.

SIR,—Having just read Mr. Dunn's letter (CHEMICAL NEWS, vol. civ., p. 221), being a reply to Mr. Bryant's communication concerning a "new form" of the so-called Ostwald's apparatus for purifying mercury, may I be allowed to observe that the invention of Mr. Bryant is really the original form of the purifier, and is described in all text-books on laboratory manipulations (e.g., Ostwald's "Hilfs und Handbuch," three editions; Travers' "Experimental Study of Gases," English edition, p. 16; German version of the same, p. 16, &c.), as well as in the catalogues of the leading firms both in England and the Continent (e.g., Baird and Tatlock; Desaga, in Heidelberg; Dr. Bender and Dr. Hobein, in Munich; F. Köhler, in Leipzig, formerly in Ostwald's laboratory; Vereinigte Fabriken in Berlin, &c.). Never and nowhere could I find a mention of using wash-leather in contact with nitric acid.

As both Mr. Bryant and Mr. Dunn are of the opinion that the apparatus is very efficient, may I point out that its efficiency can be increased nearly forty times by substituting Dr. Palmar's funnel for the common one as described, among others, by Mr. Bryant. Dr. Palmar's funnel (vide *Ber.*, 1899, p. 1381) is stopped at the lower end by means of a ground-in glass rod; this surface of contact contains about forty fine vertical scratches, so that the mercury flows out in about forty fine streams instead of one. Besides, the fine opening of the drawn-

out funnel tube becomes very easily stopped by dirt, dust, or mercuric nitrite crystals, and is only very difficultly cleansed, whereas Dr. Palmar's funnel can be instantly cleaned by simply taking out the rod.—I am, &c.,

TAD. ESTREICHER,

Professor of the Fribourg University, Ph.D.

Université de Fribourg (Suisse),
Laboratoire de Chimie II.

MEMORIAL TO DR. JOSEPH PRIESTLEY.

To the Editor of the Chemical News.

SIR,—The movement to commemorate in his native town of Birstall the distinguished scientific discoverer and philosopher, Dr. Joseph Priestley, has so far had its chief support from local sympathisers only. Yet that so illustrious and world-famous a man—"a type of the intellectual energy of the eighteenth century," according to Mr. Frederick Harrison—should no longer lack a fitting Memorial in the town of his birth, will commend itself to all who know his story, and the Executive Committee, under the presidency of W. Middlebrook, Esq., M.P., ex-Lord Mayor of Leeds, now feel that the time has come for appealing through the Press to a wider public. We are sure that there must be among the many readers of your paper a number of admirers of "the hero of the eighteenth century" who will welcome an opportunity to aid the present effort.

It has been decided that the Memorial shall take the form of a life-size bronze statue in the Market Square, and the Committee consider that the total cost, including a suitable pedestal and inscription, will not fall short of £1000. Towards this amount about £450 has already been secured, and appeal for contributions is hereby made to every lover of science and admirer of philosophical inquiry.

An illustrated booklet has been prepared, and will be forwarded on request. Donations may be sent direct to "The Priestley Fund," London City and Midland Bank, Batley, or to the Hon. Treasurer, Walter Bagshaw, Esq., J.P., F.R.M.S., Moorfield House, Birkenshaw, Bradford.—(On behalf of the Committee). Yours faithfully,

W. ORLANDO R. HOLTON, Chairman of the
Birstall Urban District Council.

ARTHUR PORRITT, Hon. Secretary of the
Executive Committee.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlv., No. 14, 1911.

Studies of Absorption Spectra.—A. W. Stewart and Robert Wright.—When iodine is dissolved in alcohol the power of the solution of absorbing light increases relatively more than would be expected from the increasing dilution. This is probably due to the formation of an addition product between iodine and alcohol. The same phenomenon is observed when *p*-nitro-toluol is dissolved in alcohol. When iodine is dissolved in water exactly the opposite occurs; hence possibly an oxonium derivative is formed, and is then ionised by dilution. Solutions of iodine in mixtures of water and alcohol can be made more transparent to light by increasing the percentage of water, and more absorbent by increasing the percentage of alcohol. Azobenzene, which is incapable of forming addition products, and also of ionisation, obeys Beer's law both in alcoholic and aqueous alcoholic solution.

Ferromagnetic Compounds of Manganese with Phosphorus, Arsenic, Antimony, and Bismuth.—Siegfried Hilpert and Theodor Dieckmann.—Manganese phosphide can be prepared by heating manganese and red phosphorus to 600° in a pressure tube, and the antimonide and bismuthide by heating manganese amalgam with the powdered metal in a current of hydrogen. The temperatures at which the products lose their magnetisability are as follows: —MnP, 18—26°; MnAs, 40—45°; MnSb, 320—330°; MnBi, 360—380°. Thus the temperature rises with the atomic weight of the element combined with the manganese.

MEETINGS FOR THE WEEK.

- MONDAY, 4th.—Royal Society of Arts, 8. (Cantor Lecture). "The Carbonisation of Coal," by Prof. Vivian B. Lewes
- Society of Chemical Industry, 8. "Physical Properties of Clays," by W. C. Hancock. "The Value of the Non-tannins in the Formation of Leather," by Dr. J. Gordon Parker and J. R. Blockey. "Estimation of Carbon Monoxide," by L. A. Levy. "Composition of Bassia Fats," by R. G. Pelly.
- Royal Institution, 5. General Monthly Meeting.
- WEDNESDAY, 6th. Royal Society of Arts, 8. "British Guiana and its Founder, Storm van 's Gravesande," by J. A. J. de Villiers.
- Society of Public Analysts, 8. "Estimation of Small Quantities of Essential Oil in Spices, &c.," by J. A. Brown. "Determination of Furfural by means of Fehling's Solution," by L. Eynon and J. H. Lane. "Examination of Petroleum Mixtures," by J. H. Coste, E. T. Shelbourne, and E. R. Andrews. "Ground Almonds," by G. C. Jones and R. F. Easton. "Method for Determining the Amount of Insoluble Particles in Raw Rubber," by C. Beadle and H. P. Stevens. "Determination of Small Quantities of Methyl Alcohol," by C. Simmonds. "Oil of Male Fern," by E. J. Parry. "Composition of Australian (Victoria) Milk," "The Composition of Sweetened Condensed Milk," and "The Aldehyde Figure of Butter," by E. H. Miller.
- Faraday Society, 8. "Re-determination of the Density and Coefficient of Linear Expansion of Aluminium," by F. J. Brisslee. "Solution Volumes of Nitric Acid," by V. H. Veley. "Influence of the Physical Condition of Metals on Cathodic Over-voltage," by J. N. Pring and J. R. Curzon. "Notes on Thermostats," by H. Marshall. "Notes on Two Thermo-regulators," by W. R. Bousfield. "Notes on Thermostats and Devices Used in connection with Thermostats," by A. C. Cumming. "Exhibition of Thermostats. Exhibition of Silica Mercury Lamps for Spectroscopic and Polarimetric Work," by T. M. Lowry. "Exhibition of the latest form of the Benko Primary Battery," by W. R. Cooper.
- THURSDAY, 7th.—Royal Society. "Lapworthura—a Typical Brinellstar of the Silurian Age, with Suggestions for a New Classification of the Ophiuroidea," by Miss I. B. and Prof. W. J. Sollas. "Physiological Influence of Ozone," by Dr. L. Hill and M. Flack. "Factors concerned in Agglutination," by H. R. Dean. "Action of Dissolved Substances upon the Auto-fermentation of Yeast," by Dr. A. Harden and S. G. Paine. "Further Experiments upon the Blood Volume of Mammals and its Relation to the Surface Area of the Body," by G. Dreyer and W. Ray. "Origin and Destiny of Cholesterol in the Animal Organism—Part VIII.. On the Cholesterol content of the Liver of Rabbits under various Diets and during Inanition," by G. W. Ellis and J. A. Gardner.
- Chemical, 8.30. "Chemical Examination of the Root of *Ipomoea orizaeensis*," by F. B. Power and H. Rogerson. "Constitution of Ergothioneine, a Betaine related to Histidine," by G. Barger and A. J. Ewins. "The Methane Equilibrium," by J. N. Pring and D. M. Fairlie. "Absorption of the Halogens by Dry Slaked Lime," by W. A. R. Wilks. "Decomposition of Nitric Acid by Light" and "Presence of Iodic Acid in Commercial Pure Nitric Acid," by W. C. Reynolds and W. H. Taylor. "Method of Determining Carbon and Nitrogen in Organic Compounds," by E. P. Frankland. "Derivatives of *o*-Xylene—Part I., 3-Nitro-*o*-xylene and 3:6-Dinitro-*o*-xylene," by A. W. Crossley and Miss G. H. Wren. "Derivatives of *o*-Xylene—Part II., Dinitroamino-*o*-xylene," by A. W. Crossley and G. F. Morrell. "Diphenylcyclopentenone," by S. Ruhemann and W. J. S. Naunton. "Electrolytic Reduction—V., Benzylidene Bases," by H. D. Law.

MACMILLAN'S NEW and RECENT BOOKS ON CHEMISTRY.

NEW EDITION, Completely Revised.

A TREATISE ON CHEMISTRY.

BY

The Rt. Hon. Sir H. E. ROSCOE, F.R.S.,

AND

C. SCHORLEMMER, F.R.S.

VOL. I.—The NON-METALLIC ELEMENTS. Fourth Edition. Completely Revised by Sir H. E. ROSCOE, F.R.S., assisted by Dr. J. C. CAIN. Illustrated. 8vo. 21s. net.

VOL. II.—The METALS. New Edition. Completely Revised by Sir H. E. ROSCOE, F.R.S., and A. HARDEN, F.R.S. 8vo. 30s. net.

CLASS BOOK OF CHEMISTRY.

By G. C. DONINGTON, M.A. Part I., 1s. 6d.; Parts II. and III., 2s. 6d.; Complete, 3s. 6d.

All the subjects included in the new syllabus in Chemistry for the Matriculation Examination of the University of London are dealt with in this book.

SCHOOL WORLD.—"The volume is most appropriate for classes in secondary schools and for junior classes in technical schools, and it possesses the advantage of meeting the requirements of both class-room and laboratory. The experiments are quite simple, and frequently exhibit novelty of method combined with improved efficiency. The illustrations are excellent."

Chemistry. An Elementary

Text-book. By WILLIAM C. MORGAN, Ph.D., and JAMES A. LYMAN, Ph.D. Crown 8vo. 5s. 6d. net.

THIRD EDITION.

NOW READY.

ESSAYS IN HISTORICAL CHEMISTRY

By Sir EDWARD THORPE, C.B., LL.D., F.R.S., &c. 8vo. 12s. net.

Contains Lives of R. Boyle, J. Priestley, C. W. Scheele, H. Cavendish, J. Watt, A. L. Lavoisier, M. Faraday, T. Graham, F. Wöhler, J. B. A. Dumas, H. Kopp, V. Meyer, D. I. Mendeléeff, S. Cannizzaro, and J. Thomsen.

THIRD ENGLISH EDITION.

Theoretical Chemistry

from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. WALTER NERNST, Ph.D. Revised in accordance with the Sixth German Edition by H. T. TIZARD. Third English Edition. 8vo. 15s. net.

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. CIV., No. 2715.

NOTE ON THE APPROXIMATE ESTIMATION OF STARCH BY IODINE.

By LESTER REED, F.I.C.

I HAVE found the following method to give approximate results in mixtures containing starch not previously heated:—

Such a quantity of substance is worked on as will contain about 0.1 grm. of starch. This is heated to 190° C. with about 5 cc. of glycerin for five minutes. The solution of starch in glycerin is then diluted to about 50 cc., and filtered with aid of filter-pump and steam jacket. An ordinary German filter with platinum cone is better than a hardened filter. The cold solution is next precipitated with a strong solution of iodine in 10 per cent KI solution. The precipitated iodide of starch should be granular. After standing it is collected on a fluted filter (previously moistened with water containing I+KI), then washed with boiling 90 per cent alcohol. The filter is next spread on a glass plate, and the precipitate washed into platinum dish with a jet of boiling water. The contents of platinum dish are boiled to expel iodine, and afterwards evaporated over water-bath to constant weight, and corrected for ash.

A sample of starch gave 80 against 83.7 theory. A mixture of starch and fat-free mustard gave 43 against 41.8 theory. A sample of flour showed 70 per cent of starch.

The highest accuracy is not claimed for this process at its present stage, and it entirely fails with bread and cocoa. In the former the precipitate cannot be filtered off, and in the latter theobromine or some other substance appears to be precipitated.

THE COOKING AND CHEMICAL COMPOSITION OF SOME ENGLISH FISH.

By KATHARINE I. WILLIAMS, B.Sc.

IN a previous paper on "The Composition of Cooked Fish" (*Trans. Chem. Soc.*, 1897) full details were given of the methods of analysis of the flesh of some of the best-known English fish. The main object of this work was to obtain information regarding the composition of foods as served at table, little being known as to the changes produced during the process of cooking.

It is interesting to observe that some varieties of fish are common both in England and the United States of America, such as salmon, cod, hake, halibut, herrings, turbot, and mackerel, while lemon and other kinds of soles, gurnet, and brill are not on the list of edible fish given in *Bull.* 28, Office of Experiment Station; on the other hand, cusk, blue-fish, black-fish, and alwife are unknown in England.

All the samples used were purchased when in full season; cod, lemon soles, and turbot came from Grimsby, and, excepting trout, the others were procured from local fish-mongers. A sample of tinned salmon was also included, which was marked "spring catch" from Columbia River, Stag Brand, Rob Roy Packing Co.

General Preparation of the Samples.

In some cases the fish was sent from the shop ready for cooking, in most the usual method of preparation was followed. The following table gives the per cent of waste material:—

Percentage of "offal."

Eels	25.0
Red mullet	11.1
Gurnet	9.1
Brill	12.1
Halibut	9.9
John Dory	21.5
Roach	31.2

Details as to Preparation.

Plaice.—This sample was fully prepared for cooking, all bones being removed.

Salt Herrings.—Only the edible portion of the fish was used, the bones and heads being first removed, the sample being well soaked in cold water to remove a portion of the salt before the process of cooking was commenced.

Salt Cod.—The section used was also well soaked to remove the excess of salt.

With varieties such as trout, whiting, and smelts, the entire samples were used; with large fish such as cod, salmon, and brill only a section was cooked.

General Method of Cooking.

The prepared samples of fish were boiled in undistilled water, as supplied by the Bristol Water Co., which showed 26° of hardness, mainly due to calcium carbonate. Every sample was weighed before and after cooking, and in every case a decrease in weight was observed, a fact the reverse of the effect of cooking on almost all vegetable foods and cereals, as shown in "The Chemical Composition of Cooked Vegetable Foods," Parts I. and II. (*Journ. Am. Chem. Soc.*, vol. xxvi, No. 3, and vol. xxix., No. 4).

Table I. shows the decrease in weight, the price of the raw article, the weight of the refuse (skin, bones, and heads) removed after cooking, the date of purchase, if whole or only a section of the fish was selected, the edible portion of flesh left for analysis.

The price quoted per pound can only be taken as representing the Bristol market, and may be higher or lower in other towns according to circumstances.

Prof. Grindley describes in detail a series of investigations with meat in "Experiments on Losses in Cooking Meats" (*Bull.* 141, Office Experiment Stations). The average weight of the pork hams used was 1151.96 grms., of beef 1867.07 grms.; his work gives the result of a total of eighty-seven samples, going into full details as to the various methods of cooking, weight of samples before and after. In this work on fish, the method of cooking was plain boiling, and the weight used was considerably less: lemon soles, 790.7; whiting, 935; fresh herrings, 471.5 grms. In every case a loss of weight in cooking is observed. (See Table II.)

In summing up his investigations, Prof. Grindley states, as the result of thirty-two roasting experiments, the loss of weight varied from 12.68 to 46.21 per cent, giving an average of 26.82 per cent; in the forty-two boiling experiments the loss of weight varied from 10 to 50 per cent, with an average of 34.35. No two samples of the same variety of fish would be exactly alike in their composition. It may be mentioned that in cases like herrings, sprats, and smelts the results given are the average of several samples, while with moderate sized fish, such as gurnet and John Dory, only one specimen was used; with larger fish, such as cod, salmon, and hake, only a portion could be used, but in every case precautions were taken to procure sufficient for the purpose of the complete analysis. The loss of weight on cooking varied from 6.2 per cent to 35 per cent, but eliminating the small loss in the case of smelts the average of the twenty-two is 23.5 per cent. In order to see whether any food material could be obtained from the "waste," all the bones, head, and skin were carefully removed and weighed (the results are shown in Table I.). This refuse was crushed with a pestle and mortar, boiled in distilled water, the filtrate syphoned off, and evaporated over a water-bath until the weight of the

TABLE I.

TABLE I.						As served at table.	
Price per pound.	Date.	Portion analysed.	Weight before cooking.	Weight after cooking.	Waste, bones, &c.	Flesh portion.	
Pence.			Grms.	Grms.	Per cent.	Per cent.	
Herring	2½	February	Whole	100	64·3	12·4	87·6
Salt herring	1¾	January	Flesh	100	71·4	—	100
Sprats	3	November	Whole	100	71·8	18·80	81·2
Salmon	16½	July	Section	100	77·0	6·5	93·5
Salmon peel	14	July	Section of body and head	100	71·7	18·1	81·9
Trout	22	May	Whole	100	67·5	8·8	91·2
Smelts	18	March	Whole	100	93·8	19·2	80·8
California salmon .	10½	Spring catch	Flesh from section	100	—	—	100
Eels	13	October	Heads removed	100	80·9	12·8	87·2
Red mullet	22	February	Whole	100	83·3	26·7	73·3
Roach	6	January	Whole	100	78·0	25·0	75·1
Gurnet	5	February	Whole	100	68·3	47·0	53·0
Mackerel	8	April	Whole	100	87·7	10·8	89·2
Cod	8	January	Section	100	72·1	16·4	83·6
Salt cod	6	February	Section	100	73·9	6·5	93·5
Haddock	5	January	Whole	100	58·7	35·9	64·1
Whiting	7	January	Whole	100	78·8	22·4	77·6
Hake	6	February	Section	100	74·5	8·1	91·9
Turbot	18	February	Anterior and head	100	83·7	31·8	68·2
Brill	14	March	Section	100	80·6	8·4	91·6
Halibut	12	May	Section	100	74·8	6·9	93·1
Plaice	7	December	Flesh	—	—	—	100
Soles	23	March	Whole	100	82·5	22·8	77·2
Lemon soles .. .	11	January	Whole	100	84·3	27·6	72·4
John Dory	6	June	Whole	100	86·5	21·9	78·1

TABLE II.—Loss in Weight of Cooking.

	Per cent.
Herrings	35·7
Salt herrings	22·6
Sprats	28·2
Salmon	23·0
Salmon peel	28·3
Trout	32·5
Smelts	6·2
Eels	19·1
Red mullet	16·7
Roach	22·0
Gurnet	31·7
Mackerel	12·3
Cod	27·9
Salt cod	26·1
Haddock	41·3
Whiting	21·2
Hake	25·5
Brill	19·3
Halibut	25·2
Soles	17·5
Lemon soles	15·7
John Dory	13·5
Turbot	16·3

TABLE III.—Gelatin from Waste.

	Per cent.
Herrings	4·99
Sprats	4·85
Salmon	8·08
Salmon peel	1·14
Trout	5·89
Smelts	1·99
Eels	8·64
Hake	3·26
Red mullet	9·23
Roach	2·60
Gurnet	1·38
Mackerel	2·35
Cod	2·64
Salt cod	4·91
Haddock	2·24
Whiting	3·77
Turbot	2·34
Brill	1·79
Halibut	0·23
Soles	3·27
Lemon soles	5·16
John Dory	4·49

residue was constant; this was weighed as gelatin. Table III. gives the result.

Methods of Analysis.

As before stated, the methods employed are fully described in "The Composition of Cooked Fish" (*Trans. Chem. Soc.*, 1897). As there stated, every sample of the flesh of the fish was broken up into small pieces, surface water removed before the process of drying was commenced. The drying was first carried out in a steam bath, and then in an air-bath at a temperature not exceeding 110°. When this process was finished the sample was reduced to as fine a powder as possible in a coffee-mill, but with fish containing high percentages of fat this method was impossible, and it was found that crushing in a mortar gave satisfactory results. The powders were kept in bottles with close fitting stoppers, and used for the other determinations, such as ash, fat, nitrogen, reducing substances,

sulphur, and phosphorus. Table VI. shows the proximate analysis for the flesh in its natural moist condition as served at table.

The question of phosphorus from the point of view of nutrition is considered by many as of considerable importance, and a widespread notion exists that fish is a valuable "brain-food" because it is rich in this element, but according to the best analysis the percentages of phosphoric anhydride are not higher in fish than in the flesh of animals. The following table gives the results of the analysis of uncooked flesh foods by Girard (*Comptes Rendus*, 1896, cxxii., 1387 :—

Vegetables—	P ₂ O ₅ (per cent.)
Carrot	0·036
Turnip	0·058
Cabbage	0·089
Potato	0·140
Chestnuts	0·200

TABLE V.

	Ash.	Protein, N $\times$ 6.25.	Fat, ether extract.	Reducing substances.	Nitrogen pentoxide.	Undetermined.
Herring	5.56	67.07	25.25	—	0.66	1.44
Salt herring	19.69	38.88	21.90	17.59	1.64	0.44
Sprats	6.42	57.94	27.37	9.88	—	—
Salmon	4.94	56.65	29.43	14.89	0.46	—
Salmon peal	3.64	41.61	43.95	13.10	—	—
Trout	6.60	80.00	8.84	4.68	—	—
Smelts	4.73	82.59	9.76	2.17	—	0.75
California salmon	5.65	56.56	34.27	4.31	—	—
Eels	2.11	42.88	44.68	8.91	—	1.42
Red mullet	5.43	66.26	24.52	9.79	1.84	—
Roach	1.08	79.14	15.03	6.28	—	—
Gurnet	3.53	89.16	1.81	14.77	—	0.73
Mackerel	4.07	62.32	25.73	13.93	0.33	—
Cod	3.31	91.55	1.15	6.67	0.63	—
Salt cod	14.26	76.06	0.94	7.14	0.31	1.29
Haddock	3.28	79.57	1.29	13.15	0.43	2.38
Hake	3.90	81.36	5.67	13.64	—	—
Whiting	1.92	79.55	1.86	17.54	—	—
Turbot	2.41	84.71	4.75	11.81	—	—
Brill	4.42	93.95	1.62	—	—	—
Halibut	4.11	79.67	15.81	—	—	0.41
Plaice	4.06	75.16	9.84	11.56	2.78	—
Soles	3.47	86.71	1.71	11.84	—	—
Lemon soles	4.42	69.88	12.96	14.80	—	—
John Dory	2.06	79.53	8.52	14.39	0.13	—

TABLE VI.—Proximate Analysis calculated for the Materials in their Natural Moist Condition.

	Water.	Ash.	Protein N $\times$ 6.25.	Fat, or ether extract.	Reducing substances.	Nitrogen pentoxide.
Herring	60.54	2.21	26.46	9.96	Trace	0.26
Salt herring	46.03	11.28	20.98	11.28	9.49	0.89
Sprats	75.77	1.56	14.03	6.63	2.39	—
Salmon	65.32	1.72	19.64	10.20	5.16	0.16
Salmon peal	40.90	2.15	24.59	25.97	7.74	—
Trout	73.58	1.74	21.13	2.33	1.23	—
Smelts	80.73	0.91	15.91	1.88	0.04	—
California salmon	61.90	2.16	21.54	13.05	1.64	—
Eels	61.08	6.82	16.68	17.38	3.45	—
Red mullet	68.26	1.72	21.02	7.78	3.10	0.59
Roach	75.37	0.26	19.49	3.70	1.54	—
Gurnet	73.77	0.93	23.38	0.47	1.25	—
Mackerel	73.13	1.09	16.74	6.91	3.76	0.09
Cod	76.32	0.76	21.67	0.27	1.58	0.15
Salt cod	72.35	3.94	21.03	0.26	1.97	0.09
Haddock	72.37	0.91	21.98	0.36	3.63	0.12
Hake	84.88	0.57	12.30	0.87	2.06	—
Whiting	78.78	0.41	16.88	0.39	3.70	—
Turbot	77.84	0.51	18.77	1.05	2.62	—
Brill	62.74	1.65	35.00	0.64	—	—
Halibut	74.46	1.05	20.34	4.04	—	—
Plaice	79.86	0.82	15.13	1.98	2.32	0.56
Soles	79.20	0.57	18.03	0.35	2.46	—
Lemon soles	78.11	0.97	15.29	2.83	3.24	—
John Dory	77.89	0.19	17.54	0.45	2.50	0.03

Animal—	P ₂ O ₅ (per cent).
Pork	0.160
Beef	0.285
Eggs	0.337
White cheese	0.374
Mutton	0.425
Gruyère cheese	1.350

	P ₂ O ₅ (per cent).
Cod	0.60
Salt cod	0.25
Eels	0.68
Haddock	0.47
Halibut	0.44
Herrings	0.55
Mackerel	0.56
Salmon	0.59
Smelts	0.81
Turbot	0.48

The following table is taken from one by Prof. Atwater in "The Report of the U.S. Commissioner of Fish and Fisheries (1888)," and gives the amount of phosphoric anhydride in the flesh of fresh fish. Only such fish are here given as are common to England and the United States.

Table IV. shows the percentage of phosphoric anhydride in the cooked fish. It will be noticed in some cases it is higher, and in some lower, than in the uncooked

samples, but differences may be expected, as no two individual varieties would be likely to agree in this respect. Salt herrings, halibut, and John Dory would be the more valuable as a source of phosphorus in a dietary. The percentage of sulphuric anhydride is also given, as attention has been turned in this direction in some of the publications of the Office of Experiment Stations. These percentages are calculated for the materials in their natural moist condition as served at table.

TABLE IV.—Phosphoric Anhydride and Sulphuric Anhydride.

	SO ₃ (per cent).	P ₂ O ₅ (per cent).
Herrings	0.43	0.82
Salt herrings	0.85	1.09
Sprats	0.34	0.64
Salmon	0.35	0.41
Salmon peel	0.57	0.78
Trout	0.73	0.69
Smelts	0.31	0.41
California salmon ..	0.45	0.51
Eels	0.43	0.37
Red mullet	0.52	0.25
Roach	0.63	0.51
Mackerel	0.22	0.53
Gurnet	0.42	0.27
Cod	0.32	0.34
Salt cod	0.44	0.48
Haddock	0.52	0.87
Whiting	0.47	0.37
Hake	0.26	0.27
Turbot	0.27	0.30
Brill	0.68	0.59
Halibut	0.40	1.04
Plaice	0.26	0.32
Soles	0.33	0.25
Lemon soles	0.28	0.27
John Dory	0.52	1.33

The main object of these investigations was to obtain a clearer knowledge of the composition of cooked foods as served at table, as most of the work on the subject deals with the uncooked material.

Table V. gives full details of the analysis of the dried fish powders obtained in the manner previously described; it shows the percentages of ash, protein (calculated from nitrogen), fats, reducing substances (reckoned as glucose), also of nitrogen pentoxide (estimated by modification of Schloësing method). Table VI. gives the proximate analysis calculated on the materials in their natural moist condition, in order to show clearly the true nutritive value of the foods under consideration.

It will be observed that there is a considerable variation in the percentage of fat in the various kinds of fish, from 24.59 in the case of salmon peel to 0.26 salt cod; meats show also considerable variation in this respect, but as a rule contain more fat even in the cooked condition.

Compared with meat, however, the percentage of refuse (skin, bones, &c.) is greater with fish obtained from the market; also the proportion of water is higher both in the cooked and uncooked condition, but as a source of protein material fish holds its own. It is unfortunate from an economic point of view that the price of some varieties should show a tendency in England to rise, although it may be pointed out that the inexpensive herring is a cheap and valuable source of protein food-stuff.

The University of Bristol.

2. 3 and 3. 4-Dioxy-benzylamines. — R. Douetteau. —The author has prepared these two bases by methylating the corresponding vanillins, transforming the products into oximes, and then reducing. Thus the methyl ethers of the amines are formed, and can be demethylated by means of hydriodic acid.—*Bull. Soc. Chim. de France*, ix.-x., Nos. 20—21.

ON THE CONSTANCY OF THE SULPHUR BOILING-POINT.

By C. W. WADNER and C. K. BURGESS.

IN view of the general use and convenience of the sulphur boiling-point as a temperature for the standardisation of thermometric apparatus, it is highly desirable to demonstrate conclusively by experiment that we are really dealing with a strictly reproducible and satisfactorily constant temperature throughout the column of vapour in the standard form of sulphur boiling apparatus, which is generally used.

We have recently shown (*Bulletin Bureau of Standards*, 1910, vi., p. 149) that in the ordinary form of Callendar and Griffiths apparatus, in which the sulphur is boiled in a glass tube some 45 cm. long by 4.5 cm. diameter, heated from below either electrically or by a gas burner, and in which the thermometer coil, mounted within a porcelain tube glazed on the outside, is enclosed in a cylindrical or conical radiation shield of aluminium of some 15 cm. in length, the temperature of the sulphur vapour, as measured with resistance thermometers having coils 4 to 5 cm. long, is apparently constant to within 0.03° C. throughout some 27 cm. of the 30 cm. length of the column of sulphur vapour.

With thermo-couples of platinum-rhodium and of platinum-iridium, however, discordant results were obtained, varying both with the couple and depth of immersion of the wires in the vapour, and indicating an apparent point-to-point variation within the radiation shield of the order of 0.5° C.

Since it might be maintained that the relatively long resistance thermometer is an integrating device giving an average temperature within the shield whose real temperature would be far from constant as shown by the thermo-couples which presumably give the temperature at a point, we have thought it worth while to endeavour to remove any existing doubts as to the constancy of the temperature of sulphur vapour in this apparatus by further experiments.

It should first be noted, perhaps, that the resistance thermometer, if it can be made small enough, is more suited than the thermo-couple for the measurement of small differences in temperature at the sulphur point, as the indications of the former, read as a strictly potential instrument, may be freed from any thermo-electric phenomena occurring in the lead wires; whereas, in the case of the latter, such effects are additive, and when they occur in the platinum or alloy leads cannot be distinguished from the E.M.F. of the junction.

We have therefore used, for the exploration of the temperature in the sulphur apparatus, in addition to several thermo-couples, a resistance thermometer of very short coil, less than 9 mm. in length. Its resistance at the sulphur boiling-point was about 13.1 ohms, the measuring current 0.006 ampères, causing a rise of less than 0.01° C. in the temperature of the thermometer coil. The potential terminal method of measurement was used (see above reference), permitting changes of less than 0.02° C. to be detected with certainty.

Using either the cylindrical or conical radiation shield, with umbrella top to eliminate condensation cooling, and taking measurements at various depths of immersion in the vapour, and for all positions within the shields up to 2 cm. of the top, no variations as great as 0.05° C. were observed. In the following table, for example, are given the results on two series of measurements for the distribution within the cylindrical shield, the zero position being at the lowest position in the shield corresponding to the bottom of the long resistance thermometers previously used.

Distance thermometer raised, in cm.	Resistance of thermometer.	
	Depth of immersion of shield in S vapour.	
	25 cm.	28 cm.
0	13.128	13.126
5	13.127	13.126
10	13.128 ₅	13.127

Outside the radiation shield, of course, the temperature falls off rapidly due to the cooling effect of the liquid running down the tube and to radiation.

Various thermo-couples of wire 0.6 mm. diameter and which had been subjected to high temperature usage were tried, with results varying from 0.0° to 1.0° for the apparent range of temperature within the shield. Even with a differential thermo-couple, a distribution differing by several tenths degree was obtained according as one junction or the other was raised. The most uniform distribution was found with couples which had been used the least at high temperatures. Finally, in order to eliminate the effects both of conductivity and of heterogeneity in the wires, we used a couple of which the wires were 0.1 mm. diameter, and which had been annealed and calibrated once, but not otherwise used. With this very fine and electrically homogeneous thermo-couple, most satisfactory results were obtained for the temperature distribution in the shield as shown below for an immersion of 27 cm.

Distance couple raised, in cm.	Change in temperature, °C.
2	+0.03
4	0
6	0
5	+0.01
7	+0.01
9	-0.03
11	+0.04
3	+0.06
6	+0.02
9	-0.04
5	+0.02
&c.	&c.

These variations are of the order of the error of measurement and of barometric fluctuations.

It appears to be proved therefore by a point-to-point exploration within the radiation shield of the standard form of sulphur boiling-point apparatus by means of suitable resistance and thermo-electric thermometers, and for any position of the shield throughout nearly the whole length of the sulphur vapour column, that the temperature is certainly constant to within 0.05°, and probably within 0.03° C.

As shown previously (Waidner and Burgess, *Bulletin Bureau of Standards*, 1910, vii., p. 3), the most probable numerical value of the sulphur boiling-point on the scale of the constant volume nitrogen thermometer, as deduced from all the available data, is 444.7° to within 0.1° C., with a variation of about 0.00° per mm. Hg change in pressure.

In spite of the complexity of sulphur in its chemical behaviour, such as possessing several valencies and isomeric forms in the solid and liquid states, the fixity of the temperature of its vapour during boiling appears to be all that could be desired. It would seem that the only phenomenon that could cause this constancy to be questioned would be the existence of two forms of liquid sulphur of slightly different boiling-points, and one form gradually changing into the other with continued boiling. We have never been able to detect any such progressive change in the boiling-point over several hours' time. A further test of the constancy of this temperature is the remarkably close agreement on extrapolation to such high temperatures as the silver and copper points (*loc. cit.*) using for calibration sulphur that had been re-boiled many and few times.

We may therefore say with a considerable degree of positiveness that the temperature defined by the sulphur boiling-point apparatus may readily be reproduced to within 0.05° with reasonable care; and as compared with the fixed points either temperatures of freezing or boiling, given by any of the chemical elements, the sulphur boiling-point is the one the most exactly defined, the most certainly reproducible, and the most constant yet studied. —*Bulletin of the Bureau of Standards*, Washington, vii., No. 1.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 23rd, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"The Iron Flame Spectrum and those of Sun-spots and Lower-type Stars." By Sir NORMAN LOCKYER, K.C.B., F.R.S.

Previous publications are referred to indicating that the spectral lines of the metallic elements have been separated into two series, one seen best in the hotter stars and when high temperature and great electric energy are employed. These were termed "enhanced lines." The other set, existing in stars of the solar type, but not in high temperature stars, and seen with lower degrees of heat and electric energy in the laboratory, were called "arc lines." These lines have been shown to be strengthened in sun-spot spectra, while the enhanced lines are weakened.

It seemed important to consider as a third term the spectrum given by the comparatively low temperature of the oxy-hydrogen flame, and see how the lines in the spectrum behave in the spectra of sun-spots and lower-type stars.

Photographs have been recently obtained of the oxy-hydrogen flame spectrum of iron, using greater dispersion than has hitherto been employed on that spectrum at Kensington. It has been found that the lines existing in the flame spectrum nearly all behave in a similar way in sun-spot spectra, these lines being extensively winged in passing from the Fraunhoferic spectrum to the sun-spot spectrum, and, generally speaking, more conspicuous in the latter.

It has also been found that the flame lines are just those which are relatively strong in the electric furnace spectra of iron, the spectrum furnished by the lowest temperature conditions dealt with in the furnace being almost identical with the oxy-hydrogen flame spectrum.

With regard to the behaviour of the flame lines in the spectra of lower-type stars, it is found that in the region γ 4000 to λ 4330 they are mainly unaffected in the spectrum of Arcturus. In the region λ 4330 to λ 4500 the evidence tends to show that most of the lines are strengthened both in Arcturus and α -Orionis, but this point cannot be definitely established until stellar spectra of greater dispersion are available.

"*Sinhalese Iron of Ancient Origin.*" By Sir ROBERT HADFIELD, F.R.S.

There being little definite evidence regarding ancient iron, the author describes some specimens from the buried cities of Ceylon. His paper supplements one by Dr. G. Pearson, read to the Society in 1795, on Indian steel of modern manufacture.

The specimens investigated, obtained through the kindness of the Governor-General of Ceylon, Sir Henry McCallum, are—(1) a steel chisel, fifth century A.D.; (2) an ancient nail, probably of same place and date; (3) a bill-hook. This date has been verified by one of our Fellows, Dr. A. Willey, F.R.S.

Examination of the chisel showed the following composition (sp. gr. 7.60):—

	Per cent.
C	Traces
Si	0.12
S	0.003
P	0.28
Mn	Nil
Fe	99.3

Difference being slag and oxide.

Frémont shear test showed 16 tons per square inch elastic limit, 26 tons per square inch breaking load. Shock test showed 17 kg. with 85° bend before breaking. Brinell

ball test showed hardness numbers 144 and 144 on opposite sides. Scleroscopic hardness, 35. Transverse section shows the specimen to be somewhat carbonised, with carbonised areas on two sides. The presence of martensite and hardenite suggests the important information that the chisel was quenched.

The analyses in the paper probably represent the only modern complete determination of the composition of authentic specimens of ancient iron. The percentage of phosphorus, though high, does not greatly differ from modern bar iron. Sulphur is extremely low, showing the employment of a very pure fuel. There is very little silicon, while manganese is entirely absent, which is somewhat remarkable since nearly all iron contains some manganese.

From microscopical examination and other tests it results that the specimens represent wrought iron rather than steel. They somewhat resemble puddled iron, and seem to have been made from rather impure ore. The percentage of carbon is low, as is the case for other impurities with the exception of phosphorus. Slag is present in considerable quantity in a lumpy irregular form, indicating that the material was not submitted to the amount of forging undergone by modern wrought iron.

"Conductivity of a Gas between Parallel Plate Electrodes when the Current approaches the Maximum Value." By Prof. J. S. TOWNSEND, F.R.S.

"Spectroscopic Investigations in connection with the Active Modification of Nitrogen. II, Spectra of Elements and Compounds excited by the Nitrogen." By Hon. R. J. STRUTT, F.R.S., and A. FOWLER, F.R.S.

The chief results are as follows:—

1. The spectra generated by the nitrogen afterglow do not differ fundamentally from those which can be produced by other means of excitation. In many cases, however, band spectra are better displayed, and the more refrangible parts of the spectrum are more completely developed. The method therefore adds to our resources for the production of spectra.

2. The spectra of metallic substances approximate to those obtained in the electric arc, or are intermediate between arc and flame spectra.

3. The band spectra given by iodine, chloride of tin, and mercuric iodide are very similar to those obtained from vacuum tubes.

4. The spectra exhibited by sulphur, sulphuretted hydrogen, and carbon disulphide consist of bands which are quite distinct from those given by sulphur in a vacuum, but resemble the bands of the carbon disulphide flame in air.

5. The cyanogen spectrum which is developed in the glow by cyanogen and certain other compounds of carbon differs in several respects from that observed in the cyanogen flame or carbon arc. Some of the differences appear to be due to the production of the spectrum at a relatively low pressure in the glow. A new set of bands, occupying positions near the most refrangible edges of the violet groups, occurs in the glow spectrum, and has also been observed during the phosphorescent combustion of cyanogen in ozone.

"The Less Refrangible Spectrum of Cyanogen, and its Occurrence in the Carbon Arc." By A. FOWLER, A.R.C.S., F.R.S., and H. SHAW, A.R.C.S.

1. Revised wave-lengths are given for the bands forming the less refrangible part of the cyanogen spectrum. Numerous bands which have not previously been recorded are included.

2. The heads of the bands can be arranged in regular series similar to those constituting the first positive band spectrum of nitrogen.

3. There are considerable variations in the relative intensities of the various bands, according as the spectrum is obtained from the flame of the burning gas, from a

vacuum tube, or from the luminous glow produced by the interaction of certain compounds of carbon with active nitrogen.

4. The complex spectrum of the carbon arc in the red and yellow is almost entirely due to cyanogen.

5. The spectrum of cyanogen in the sun is not of sufficient intensity to give visible indications of the red and yellow bands.

"Monatomicity of Neon, Krypton, and Xenon." By Sir W. RAMSAY, K.C.B., F.R.S.

"Adherence of Flat Surfaces." By H. M. BUDGETT, B.A.

This paper deals with the various causes producing adherence between plane surfaces which have simply been "wring" together, and experiments are described which were carried out with specially prepared steel gauges. It is shown that the effects of atmospheric pressure and molecular attraction between the opposing faces are very slight, and that the adherence is chiefly due to the presence of a minute liquid film between the gauges. Tables are given comparing the force required to pull the gauges apart when various liquid films were present, and also comparing the readings obtained when separation occurred in air and in a vacuum. Microphotographs are shown, illustrating the distribution of a paraffin film over the steel, and proving that only a small area of the faces is covered by the liquid. The breaking strains of various liquids are estimated from microscopic measurement of the area of cross section under strain, and it is shown that the tensile strength of water approaches sixty atmospheres under these conditions.

"Resistance to the Motion of a Thread of Mercury in a Glass Tube." By G. D. WEST, B.Sc.

It is shown by theory and experiment that if a mercury index is to be moved along a glass tube of small bore with a velocity, v , the difference of pressure, P , on the two ends of the index is given by $P = 0.038/a + 81\eta v/a^2$ when a is the radius of the tube and η the coefficient of viscosity of mercury.

"Distillation of Binary Mixtures of Metals in Metals in Vacuo. Part I. Isolation of a Compound of Magnesium and Zinc." By ARTHUR JOHN BERRY, B.A.

Attempts have been made to isolate definite compounds of two metals, one of which at least is readily volatile, by distillation of the excess of the more volatile constituent; compare Heycock and Neville (*Trans. Chem. Soc.*, 1892, lxi., 914). In the present case, it has been shown that the compound $MgZn_2$ discovered by Grube (*Zeit. Anorg. Chem.*, 1906, xlix., 77) can be prepared by heating a mixture of magnesium with an excess of zinc in vacuo. The excess of zinc distils off, and the residual alloy consists of the intermetallic compound. It has further been shown that this compound can be distilled without decomposition.

"Analysis of Tidal Records for Brisbane for the Year 1908." By F. J. SELBY, M.A.

This paper gives the results of an analysis of one year's tidal records for Brisbane. The analysis was made by the method of Sir G. H. Darwin, the tidal abacus devised by him being employed. The results are generally in good agreement with those given by Rollin A. Harris for Sydney, as deduced from a year's observations of high and low waters. Using the constants given by the analysis, a curve was run off on the Indian tide-predicting machine at the National Physical Laboratory, and from a comparison of this with the actual records it was concluded that the values of the constants obtained were satisfactory.

"Herbage Studies. I. *Lotus corniculatus*, a Cyanophoric Plant." By HENRY E. ARMSTRONG, F.R.S., E. FRANKLAND ARMSTRONG, and E. HORTON.

Early in the summer last year plants of *Lotus corniculatus* growing on the Thames banks near Reading were found

to contain a cyanophoric glucoside, but hydrogen cyanide could rarely be detected in plants from various localities collected later in the season. This year specimens have been obtained from a great variety of British localities, and these have rarely been tested without obtaining positive results. The climatic conditions during the two seasons have been very different, so that the differences observed between plants grown in the two years would seem to be mainly due to climatic differences. This year plants have also been obtained from all over Europe—from Norway, France, Holland, Germany, Russia, Servia, and Italy. In no case was cyanide found in plants growing in Norway, where the conditions have been such as to favour luxuriance rather than "maturity" of growth. The specimens obtained from other European localities in a majority of cases contained cyanide. The glucoside is usually accompanied by a corresponding enzyme, but this may occur without the glucoside. Wherever collected the variety of *Lotus corniculatus* known as *major* (*uliginosus villosus*) has been found to be free from glucoside and enzyme; it would therefore seem that botanists are justified in ranking this form as a distinct species.

"A High-speed Fatigue Tester and the Endurance of Metals under Alternating Stresses of High Frequency."
By B. HOPKINSON, F.R.S.

In this apparatus the test-piece ($\frac{1}{4}$ inch diameter by 4 inches long) is fixed vertically, the lower end being attached to heavy masses. The upper end of the piece carries a weight. The weight is attracted by an electro-magnet placed above it, and excited by alternating current. The pull thus applied varies periodically between zero and a maximum value, the frequency of the variation being twice that of the current. The test-piece behaves as a spring, the lower end of which is held fixed while the upper end carries the weight, and is free to move in a vertical direction. The adjustments are such that the natural period of vertical oscillations of this system is approximately equal to the period of the varying magnetic pull which accordingly sets up large forced oscillations of its own period. By thus using the principle of resonance with a current-frequency of 60 periods per second the range of pull applied by the magnetic may be magnified from 20 to 70 times, and the stress produced in the piece can readily be made to alternate between 20 tons per square inch tension and 20 tons per square inch compression. The number of complete cycles per minute is 7200, and 1,000,000 reversals can be performed in two and a-half hours.

The test-piece is fitted with a simple form of optical extensometer whereby continuous observation can be kept of the change of length occurring in a cycle of stress. From the change of length the stress can be calculated if the piece is approximately perfectly elastic under the stress which is being applied. An independent estimate of the limits of stress can also be obtained by observing with a microscope the range of movement of the weight and calculating its acceleration from that range on the assumption (whose justification is fully discussed in the paper) that the motion is simple harmonic. These two methods of getting the stress were found to agree closely for the mild steel used in the experiments up to a range of stress of about 30 tons per square inch.

Endurance tests made in the new machine on mild steel showed that the steel would stand at least twenty million cycles of stress covering a range of 29 tons per square inch. Comparative tests of the same steel made by Dr. Stanton at the National Physical Laboratory in a direct stress testing machine giving about 1100 reversals per minute showed that at this speed the probable life of the material under the same range of 29 tons per square inch would be less than 100,000 reversals. Similar comparisons with both higher and lower ranges of stress confirmed the conclusion that at the high speed of over 7000 reversals per minute, the endurance is much greater than at 1100 reversals per minute, both in the number of cycles and in the actual time required to produce fracture.

CHEMICAL SOCIETY.

Ordinary Meeting, November 2nd, 1911.

Dr. M. O. FORSTER, D.Sc., Ph.D., F.R.S., Vice-President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Henry Garner, B.Sc., Sewage Works, Deighton, Huddersfield; Rufus Gaunt, M.Sc., Ph.D., 70, Abingdon Villas, Kensington, W.; Sant Ram Khosla, near City Kotwali, Lahore, India; Harold King, M.Sc., 161, Altmore Avenue, East Ham, E.; Geoffrey Martin, M.Sc., Ph.D., 4, Bertram Road, Hendon, N.W.; George Alfred Stokes, 60, Parkhill Road, Hampstead, N.W.

Of the following papers those marked * were read:—

*267. *"The Constituents of the Seeds of Casimiroa edulis."* By FREDERICK BELDING POWER and THOMAS CALLAN.

The material employed for this investigation consisted of the fresh seeds of *Casimiroa edulis*, La Llave, and Lejarza (Nat. Ord. *Rutaceae*), which were obtained directly from Mexico.

The kernels of the seed, representing about four-fifths of the weight of the entire material, gave abundant reactions for an alkaloid, and were found to contain an enzyme which slowly hydrolysed amygdalin.

An alcoholic extract of the kernels, when distilled in a current of steam, yielded a small amount of a pale yellow essential oil, which possessed an aromatic odour and the following constants:— D_{20} 0.9574; n_D^{20} 1.4525 in a 25 mm. tube.

From the portion of the extract which was soluble in water there were isolated:—(1) a new alkaloid, *casimiroine*, $C_{24}H_{20}O_8N_2$ (m. p. 196–197°), which on heating with alkalis undergoes hydrolysis with the elimination of carbon dioxide, yielding a new base, *casimiroitine*, $C_{23}H_{22}O_7N_2$ (m. p. 171°); (2) a new alkaloid, *casimiroedine*, $C_{17}H_{14}O_5N_2$ (m. p. 222–223°); (3) benzoic acid, with apparently a trace of salicylic acid. The aqueous liquid contained, furthermore, a quantity of sugar, which yielded *d*-phenyl-glucosazone (m. p. 205–207°).

The portion of the extract which was insoluble in water consisted of a soft oily resin, from which the following compounds were isolated:—(1) sitosterol, $C_{27}H_{46}O$; (2) ipuranol, $C_{23}H_{38}O_2(OH)_2$; (3) a mixture of fatty acids; (4) a new lactone, *casimirolid*, $C_{24}H_{28}O_6$ (m. p. 229–230°), which yield a new hydroxy-acid, designated as *casimiroic acid*, $C_{23}H_{28}O_4(OH) \cdot CO_2H$ (m. p. 207°), of which the silver salt, methyl ester, and acetyl derivative were prepared; (5) a yellow phenolic substance, $C_{16}H_{12}O_6$ (m. p. 215–218°).

The hypnotic or toxic properties attributed to *Casimiroa* seed could not be confirmed by physiological tests.

*268. *"Preparation of the Betaine of Tryptophan and its Identity with the Alkaloid Hypaphorine."* By PIETER VAN ROMBURGH and GEORGE BARGER.

The betaine $C_{14}H_{18}O_2N_2$ has been obtained by the methylation of tryptophan, and has been proved to be identical with the naturally occurring alkaloid hypaphorine. The intermediate compound, $C_{15}H_{21}O_2N_2$, which is formed is the quaternary iodide of methyl α -trimethylamino-*B*-indolepropionate, glistening plates, m. p. 197°.

*269. *B-2-Methoxynaphthylpropionic Acid and Methoxynaphthyl-hydrindone."* By GEORGE BARGER and WALTER WILLIAM STARLING.

Experiments were carried out with the object of adding a third six-membered ring to naphthalene by introducing a chain of three carbon atoms joining two *peri*-positions (compare Sachs and Brigl, *Ber.*, 1911, xlv., 2091). The following new substances were described:— β -2-Methoxynaphthylacrylic acid, $CH_3 \cdot O \cdot C_{10}H_6 \cdot CH \cdot CO_2H$, m. p. 160°; β -2-methoxynaphthylpropionic acid,—



m. p. 128°; and methoxyperinaphth-hydrindone, $C_{14}H_{12}O_2$, deep yellow crystals, b. p. 210°/12 mm., m. p. 135°.

*270. "Some Derivatives of 4(or 5)-Methylglyoxaline." By ARTHUR JAMES EWINS.

By heating 4(or 5)-methylglyoxaline with formaldehyde to 120°, an additive product, 4(or 5)-methyl-5(or 4)-hydroxy-methylglyoxaline, m. p. 138°, is formed. When treated with phosphoryl chloride, this compound yields 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline. The latter can be converted into 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline, m. p. 163–164°, which on reduction yields 4(or 5)-methyl-5(or 4)-β-aminoethylglyoxaline, a new base which was found to be physiologically active, having a marked vasodilator effect.

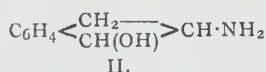
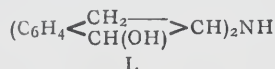
By the action of ammonia and methylamine respectively on 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline were obtained 4(or 5)-methyl-5(or 4)-aminomethylglyoxaline and 4(or 5)-methyl-5(or 4)-methylaminomethylglyoxaline. These compounds, were, however, physiologically inactive.

*271. "Studies in the Camphane Series. Part XXX. Constitution of Pernitrosocamphor (Camphenylnitroamine)." By MARTIN ONSLOW FORSTER, JOHN ROBERT TROTTER, and JACOB WEINTROUBE.

From experiments with pernitrosocamphor and its potassium derivative, the authors were led to put forward new formulæ for these compounds.

272. "Dihydroxydihydrindamine and its Resolution into Optically Active Components." By WILLIAM JACKSON POPE and JOHN READ.

Improved methods were described for the preparation of bromohydroxyhydrindene, $C_6H_4<\overset{CH_2}{\underset{CH(OH)}{>}}CHBr$, and its conversion into dihydroxydihydrindamine (I.) and 1-hydroxy-2-hydrindamine (II.) :—



The resolution of dihydroxydihydrindamine into its optically active components by means of d-camphor-β-sulphonic acid was described.

273. "Studies in Phototropy and Thermotropy. Part II. Naphthylidene-amines." By ALFRED SENIER and ROSALIND CLARKE.

The Schiff's bases obtained by the condensation of 2-hydroxy-α-naphthaldehyde with various aromatic amines have been studied in order to see if these compounds, which contain the hydroxyl radicle in the ortho-position with respect to the group ·CH:NR in the naphthalene ring, exhibit phototropy or thermotropy in the same manner as previous experience had shown to be the case with analogous benzene derivatives.

The naphthylideneamines in question are obtained by the interaction of 2-hydroxy-α-naphthaldehyde with the following amines: o-, m-, and p-chloroanilines, o-, m-, and p-bromoanilines, m-nitroaniline, o-, m-, and p-aminophenols, o-, m-, and p-anisidines, o-, m-, and p-aminobenzoic acids, o-4-, m-4-, and p-xylydines, and ψ-cumidine. None of these bases proved to be phototropic, but all exhibit thermotropy.

274. "The Stability of the Double Oxalates of Sodium and Nickel, and Sodium and Cobalt." By JOHN WALLIS DODGSON.

On boiling nickel oxalate, $NiC_2O_4 \cdot 2H_2O$, with an approximately 2N-solution of sodium carbonate, a green solution is obtained; when this is filtered from the residue, and allowed to remain for about twenty-four hours, green crystals separate, which consist of the double oxalate of sodium and nickel, with but a small amount of impurity.

The green solution cannot be crystallised by evaporation aided by heat, as the salt is partly decomposed on heating with water or with sodium carbonate solution, forming a pale green precipitate, but leaving a solution still green in colour. The green solution is also obtained when sodium oxalate and nickel oxalate are boiled together with water, and also when nickel carbonate is boiled with sodium oxalate solution, but in the latter case crystals do not form easily.

Three specimens of the crystalline compound were prepared, one (a) by boiling 20 grms. of nickel oxalate with 100 cc. of a 2N-solution of sodium carbonate, another (b) by boiling 15 grms. of nickel oxalate with 100 cc. of a 4N-solution of sodium carbonate, and a third (c) by boiling sodium oxalate and nickel oxalate in molecular proportions with water. A green solution was obtained in each case; it was filtered, and allowed to remain for a few days, when the crystals separated, and were washed several times with cold water and dried in the air. On analysis :—

(a) Found $Ni = 13.68$; $Na = 10.41$; $C_2O_4 = 41.18$; $H_2O = 34.73$ (by difference).

(b) Found $Ni = 13.62$; $Na = 10.83$; $C_2O_4 = 41.18$; $H_2O = 34.37$ (by difference).

(c) Found $Ni = 13.77$; $Na = 10.79$; $C_2O_4 = 41.43$; $H_2O = 34.01$ (by difference).

$Na_2C_2O_4, NiC_2O_4, 8H_2O$ requires $Ni = 13.82$; $Na = 10.83$; $C_2O_4 = 41.44$; $H_2O = 33.91$ per cent.

The results agree sufficiently closely with one another to warrant the conclusion that the same compound is formed in each case, and that its composition is properly expressed by the formula $Na_2C_2O_4, NiC_2O_4, 8H_2O$.

In order to test the effect of a large excess of carbonate, 100 cc. of a 4N-solution of sodium carbonate were boiled with 3 grms. of nickel oxalate; a pale green solution was obtained, from which no crystals separated after five days; later sodium carbonate crystallised out, leaving the solution still green. This result agrees with that obtained on boiling the double oxalate with a solution of sodium carbonate.

The reaction which takes place is obviously a balanced reaction, and may be represented by the equation $Na_2CO_3 + 2NiC_2O_4 \rightleftharpoons Na_2C_2O_4, NiC_2O_4 + NiCO_3$, the actual conditions of equilibrium depending on the relative masses of the sodium carbonate and nickel oxalate reacting.

As, however, the most interesting case is that of the action of a 2N-solution of sodium carbonate, 5 grms. of nickel oxalate were boiled with 50 cc. of 2N-sodium carbonate, the liquid filtered while hot, the residue thoroughly washed with successive quantities of cold water, and the filtrate and washings diluted to half a litre. Analysis showed that this contained 2.2 grms. of C_2O_4 and 0.245 gm. of nickel; these amounts are 87.5 per cent of the C_2O_4 , and 15.2 per cent of the nickel in the nickel oxalate taken. The residue left on the filter was found to contain oxalate.

Cobalt oxalate, $CoC_2O_4 \cdot 2H_2O$, is decomposed in a similar manner, but the amount of double oxalate produced is not so great. Five grms. of cobalt oxalate were boiled with 50 cc. of 2N-sodium carbonate, and filtered and washed. The filtrate was found to contain 2.37 grms. of C_2O_4 and 0.117 gm. of cobalt; in this case practically all the C_2O_4 in the original oxalate enters into solution, but only 7.3 per cent of the cobalt, as compared with 15 per cent of the nickel. The residue consisted entirely of carbonate.

The double oxalate of cobalt and sodium is easily prepared by boiling together cobalt oxalate and sodium oxalate with water. The pink solution deposits crystals on keeping, which on analysis gave the following result :—

Found : $Co = 13.89$; $C_2O_4 = 41.18$.

$Na_2C_2O_4, CoC_2O_4, 8H_2O$ requires $Co = 13.88$; $C_2O_4 = 41.41$ per cent.

It is therefore obvious that neither nickel oxalate nor cobalt oxalate can be completely converted into carbonate

by the action of a sodium carbonate solution, and that in each case a soluble double oxalate is formed, having the composition given by the formulæ already deduced, this double salt being stable in the presence of excess of sodium oxalate.

275. "The Lower Limit of Inflammation of Mixtures of the Paraffin Hydrocarbons with Air." By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

The conditions under which self-propagation of flame can take place in mixtures of inflammable gases and air were discussed. The authors find that the smallest quantity of pure methane that will enable self-propagation of flame to take place when a source of heat is introduced into a mixture of it with air is 5.6 per cent by volume of the mixture. That is to say, the "lower-limit mixture" contains 5.6 per cent of methane.

It was shown that for the paraffin hydrocarbons the lower limit of inflammation varies inversely as the calorific value of the gas. Thus, if L = the proportion of the paraffin hydrocarbon necessary to form a lower-limit mixture, and C = its calorific value, $L = f(1/c)$; or say, $L = k/c$, where k is a constant.

Using methane as the standard to obtain the value of k , the observed and calculated values of L are as follows:—

Gas.	L observed.	L calculated.
Methane	5.60 standard	5.60
Ethane	3.10	3.15
Propane	2.17	2.19
n-Butane	1.65	1.68
n-Pentane	1.37	1.36
iso-Pentane	1.32	1.36

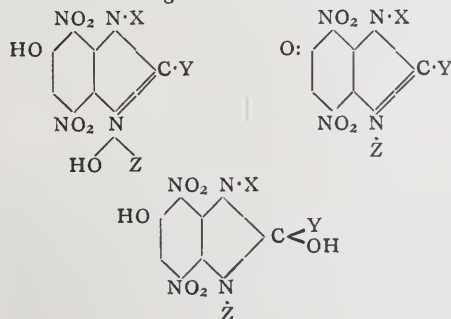
276. "Formation of Six- and Seven-membered Rings from Derivatives of 2:2'-Ditolyl." By JAMES KENNER and EMILY GERTRUDE TURNER.

Continuing their studies on the cyclic condensation of derivatives of 2:2'-ditolyl, which have been shown to lead to the formation of phenanthrene (*Proc.* xxvii., 92), the authors have found that 2:2'-dialdehydodiphenyl is converted by the action of concentrated potassium hydroxide solution into ω -hydroxy-2-methyldiphenyl-2'-carboxylic acid, m. p. 146°, from which an ϵ -lactone, m. p. 132°, is obtained by heating it at 110°.

2:2'-Ditolyl- $\omega\omega'$ -dicarboxylonitrile undergoes condensation under the influence of sodium ethoxide, with formation of 1-imino-2-cyano-3:5-dibenzo- Δ^3 :5-cycloheptadiene, m. p. 189°. This substance is hydrolysed by sulphuric acid, with formation of 1-imino-3:5-dibenzo- Δ^3 :5-cycloheptadiene-2-carboxylic acid, m. p. 180°, which yields 3:5-dibenzo- Δ^3 :5-cycloheptadiene-1-one, m. p. 78–79°, by further hydrolysis with dilute acid.

277. "Synthesis with Phenol Derivatives containing a Mobile Nitro-group. Part V. Quinoneimides, Asymmetric Quaternary Ammonium Compounds, and Asymmetric Carbinols" (continued). By RAPHAEL MELDOLA and HAROLD KUNTZEN.

The authors gave further proof of the general applicability of their method of synthesising dinitroiminazolium compounds, iminazolones, and iminazolols. A series of new compounds was described, in which the radicles X and Y in the formulæ given below had been varied:—



In the new series X represented phenyl, *p*-anisyl, *p*-chlorophenyl, and benzyl; Y = ethyl and isobutyl, and Z = methyl. A further consideration of possible formulæ for the quinoneimide compounds led the authors to maintain the correctness of their original view as expressed by the formulæ adopted. It was pointed out that the quinquivalent nitrogen atom in these compounds was comparable with that contained in compounds of the oxyammonium type, $O:N(R)_3$, the highly acid quinoid radicle representing the oxygen atom. Independent evidence of the existence of such quinoneimide compounds had been obtained in the course of a further study of the product of the extreme methylation of isopicramic acid (*Proc.*, 1910, xxvi., 232), and the authors stated that this research was in progress.

278. "Isomeric Acetaldehydephenylhydrazones." By ERNST GRAHAM LAWS and NEVIL VINCENT SIDGWICK.

Lockemann and Liesche's work on this subject has been repeated and confirmed in more detail. The hydrazone was prepared by the interaction of acetaldehyde and phenylhydrazine in aqueous alcohol. The product is a mixture of the two isomerides. The α -form, m. p. 98.6°, is obtained by re-crystallisation from alkaline aqueous alcohol, and the β , m. p. 56.6°, by re-crystallisation from acidified aqueous alcohol. Aqueous and gaseous alkalis and acids cause the isomeric change without the hydrazone passing into solution and without any apparent change in the crystals themselves.

The freezing-point curve has been obtained, and shows that the two isomerides form a continuous series of mixed crystals (solid solutions). The crystals of the two forms appear to be identical, and they have the same density. The influence of a solvent is to give an equilibrium mixture containing about 75 per cent of the α -form. The hydrazone can be distilled in a vacuum, and the isomerides pass over at temperatures 100° apart.

The peculiarity of the isomerism must be connected with the small difference in the relative stability of the two forms. On the other hand, there is no doubt that the α -modification is more stable in the presence of alkali, and the β - in the presence of acid, and that a trace of alkali or acid can bring about a change proceeding through a mass of crystals without their passing into solution. It therefore follows that there is a difference between crystals in contact with acid and crystals in contact with alkali. This can only come about by absorption of acid or alkali into the crystals, which causes a difference in energy greater than the difference between the two absolutely pure forms.

279. "Nitrites of the Alkylammonium Series. Part IV. Triethylammonium Nitrite and its Decomposition and Sublimation by Heat." By PRAFULLA CHANDRA RAY and JITENDRA NATH RAKSHIT.

Triethylammonium nitrite is obtained by the interaction of triethylamine hydrochloride and silver nitrite in aqueous solution and evaporation of the filtrate in a vacuum over sulphuric acid. The salt crystallises in pale yellow tablets and prisms. When heated it decomposes into triethylamine, alcohol, and ether, nitric oxide, nitrous oxide, and nitrogen being evolved; at the same time a portion of sublimates unchanged.

280. "The Formation of Dichlorocarbamide and its Behaviour towards Amines." By RASIK LAL DATTA.

In the preparation of dichlorocarbamide, Chattaway (*Proc. Roy. Soc.*, 1908, lxxxi., 381) ascribed the small yield which he obtained to the hydrolysis of the compound by the acid liberated in the reaction. It has now been found that during the formation of dichlorocarbamide, carbamide hydrochloride is produced, which diminishes the yield, being itself incapable of chlorination. The action of bromine on carbamide has been studied, and the results seem to point to the formation of dibromocarbamide in solution. The behaviour of amines with dichlorocarbamide has also been investigated, the result being the formation of chloroamines, with or without the evolution of gas.

281. "Synthetical Experiments in the Group of the isoQuinoline Alkaloids. Part II. The Constitution of the Condensation Products of Cotarnine and the Condensation of Cotarnine with Aliphatic and Aromatic Nitro-compounds." By EDWARD HOPE and ROBERT ROBINSON.

An account was given of the condensation of cotarnine with nitromethane, and with a number of derivatives of nitrotoluene: *o*- and *p*-nitrotoluene condense in the presence of sodium ethoxide, whilst nitromethane, di- and tri-nitrobenzenes, and also trinitroxybenzene and trinitromesitylene condense in the absence of any agent.

282. "The Synthesis of Derivatives of Thioxanthone. Part IV. Synthesis from Aromatic Sulphinic Acids." By HAROLD CHRISTOPHER and SAMUEL SMILES.

It was shown that derivatives of thioxanthone may be obtained by heating together a sulphinic acid with a *m*-hydroxy- or amino-benzoic acid. A few typical examples of this synthetical method were given. From benzenesulphinic acid and *m*-aminobenzoic acid 2-amino-thioxanthone was obtained, whilst *o*- and *p*-toluenesulphinic acids with *m*-amino- or hydroxy-benzoic acid yielded the corresponding amino- or hydroxy-thioxanthones. Hydroxy-thioxanthone, prepared by another method, was also investigated.

283. "Komppa's Synthesis of Camphoric Acid." By GUSTAVE LOUIS BLANC and JOCELYN FIELD THORPE.

The authors find that when methyl diketocamphorate is hydrolysed by very dilute alkali, that is, under conditions comparable with those used by Komppa in his synthesis of camphoric acid, the methyl group remains attached to carbon. Their criticism of this synthesis is therefore baseless.

284. "The Electrochemistry of Solutions in Acetone." Part I. By ALEXANDER ROSHDESTWENSKY and WILLIAM CUDMORE McCULLAGH LEWIS.

The object of the experiments was to find if the Nernst expressions for the electromotive forces of concentration cells hold good in acetone solution. Conductivity measurements were carried out in the case of lithium nitrate and silver nitrate in order to determine the ionic concentration values required for the calculation of the cell $\text{Ag} \left| \begin{matrix} \text{AgNO}_3 \\ \text{C}_1 \end{matrix} : \begin{matrix} \text{AgNO}_3 \\ \text{C}_2 \end{matrix} \right| \text{Ag}$, which includes in its simple form a liquid | liquid potential difference, and also for the calculation of E.M.F.'s when attempts are made to remove the liquid | liquid potential difference. The results obtained on comparing calculated and found values support the view that the simple osmotic formulæ are applicable.

285. "Chlorination of α -Naphthol by Acetylchloroamino-2:4-dichlorobenzene." By HAROLD KING.

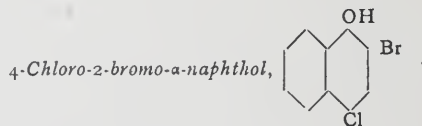
With the exception of Kast's (*Ber.*, 1911, xlv., 1337) recent preparation of 4-chloro- α -naphthol by the use of sulphuryl chloride, the four known monochloro- α -naphthols have only been obtained by indirect methods.

In investigating the direct chlorination of α -naphthol, the author has used the method described by Orton and King (*Trans.*, 1911, xcix., 1185). The naphthol is treated in glacial acetic acid solution with a molecular proportion of acetylchloroamino-2:4-dichlorobenzene and 1/100th of a gram-molecular proportion of hydrochloric acid, whereby the concentration of the chlorine set free is kept at a low value. The chlorination is rapid, and unaccompanied by oxidation. The diluted acetic acid solution is extracted with chloroform, and the latter removed by a current of warm air. The chlorinated product is separated from the accompanying dichloroacetanilide by extraction with a 2 per cent sodium hydroxide solution, and a single crystallisation from light petroleum (b. p. 60–85°) gives a 40 to 50 per cent yield of almost pure 4-chloro- α -naphthol. The exceedingly soluble residue A, recovered from the petroleum mother-liquor, corresponds in melting-point and properties with the so-called monochloronaphthol of Claus and

Oehler (*Ber.*, 1882, xv., 312), Cleve (*Ber.*, 1888, xxi., 891), and Kalle and Co. (D.R.-P. 167458). By fractional precipitation from alkaline solution by dilute mineral acid, a very partial separation into substances of different acidity takes place. (Cleve, *loc. cit.*, could obtain no pure product in this way). Nevertheless, the first 25 per cent precipitated when re-crystallised from dilute acetic acid yields hexagonal scaly crystals of α -naphthol.

2:4-Dichloro- α -naphthol, crystallising in needles, can be obtained in quantity from A by repeated crystallisation from dilute acetic acid containing 10 to 20 per cent of water. No indication of the presence of other monochloro- α -naphthols in the mixture was observed, and hence, if present, they must be very small in amount. It is seen, therefore, that the composition of the initial chlorinated product approximates to 50 per cent of 4-chloro- α -naphthol, 30 per cent of dichloro- α -naphthol, and 20 per cent of α -naphthol, the two latter obviously being present in equimolecular proportions. The determination of the melting-point curve for mixtures of α -naphthol and dichloro- α -naphthol afforded additional evidence that the soluble residue A consisted of equimolecular proportions of α -naphthol and dichloro- α -naphthol, with a very small quantity of 4-chloro- α -naphthol.

4-Chloro- α -naphthyl benzoate, $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{OBz}$ (m. p. 99–100°; Autenrieth and Mühlinghaus, *Ber.*, 1907, xl., 748, give 100–101°), was obtained by benzoylation of 4-chloro- α -naphthol. It is readily soluble in all the ordinary organic solvents, except light petroleum. (Found, $\text{Cl} = 12.46$. Calc., $\text{Cl} = 12.55$ per cent).



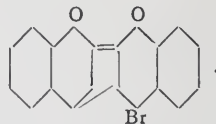
By bromination of 4-chloro- α -naphthol in acetic acid solution, 4-chloro-2-bromo- α -naphthol was obtained. It crystallises from benzene in lustrous white needles, melting at 94–95°. It is very readily soluble in the common organic solvents. From acetic acid it separates in glassy prisms, containing acetic acid, which become opaque, and disintegrate on the water-bath:—

0.1990 gave 0.2559 $\text{AgCl} + \text{AgBr}$. $\text{Cl} + \text{Br} = 44.81$.

$\text{C}_{10}\text{H}_6\text{OClBr}$ requires $\text{Cl} + \text{Br} = 44.82$ per cent.

Its constitution was proved by oxidation with fuming nitric acid, whereby 2-bromo- α -naphthoquinone and Liebermann and Schlossberg's β -dinaphthyl- α -diquinone (*Ber.*, 1899, xxxii., 548) were obtained.

4-Chloro-2-bromo- α -naphthol resembles 2:4-dichloro- and 2:4-dibromo- α -naphthol in its behaviour towards alkalis. On exposure of its solution in alkalis to sunlight, it is quantitatively converted into a deep blue insoluble substance, which still contains bromine. The fact that the ortho-bromine atom is not displaced is not in harmony with Bruncke's formula (*Diss.*, Marburg, 1903) for the corresponding compound obtained from dibromo- α -naphthol:—



Preparation of 2:4-Dichloro- α -naphthol.—The employment of two molecular proportions of acetylchloroamino-2:4-dichlorobenzene to one of α -naphthol serves as a quantitative method of obtaining dichloro- α -naphthol free from tri- and penta-chloroketona-naphthalenes which are formed when a current of chlorine is used for the chlorination.

SIR JOHN CASS TECHNICAL INSTITUTE.

THE Annual Prize Distribution of this Institute was held on Wednesday, November 29th, when the Chair was taken by Sir OWEN ROBERTS, Chairman of the Governing Body.

The Rev. J. F. MARR, Acting Chairman of the Institute Committee, first gave a *résumé* of the work of the Institute, in which he drew attention to the successful developments in the various departments of work, drawing special attention to the progress that has been made in the instruction given in applied science, particularly in Chemistry and Metallurgy, and also to the very satisfactory record of original contributions to science which have emanated from the laboratories of the Institute.

The CHAIRMAN then called upon Mr. Livingstone Sulman, the President of the Institution of Mining and Metallurgy, to deliver his address and to distribute the prizes.

Mr. SULMAN stated in his opening remarks that, in common with many other business and technical men, he had known the work of the Sir John Cass Technical Institute for a considerable number of years, and was most favourably impressed by the thoroughness and comprehensiveness of the curriculum provided in Chemistry and in Metallurgy, and by the completeness of the equipment of the Institute, not only for teaching but for that equally important branch of modern education, investigation and research.

Turning to the subject of Metallurgy, Mr. Sulman pointed out that the dominant thought which impressed one to-day was the many-sidedness, the increasing scope, and the intense vigour which now marks metallurgical progress. Of late years new conceptions seem to have infused themselves throughout the so-called inorganic sciences, and to have re-animated them, with the result that inorganic chemistry, physics, and mathematics have been imbued with a new vitality. The interaction of associated sciences is now beginning to play its part in the development of metallurgical industries. Certain of the factors of so-called molecular energy find expression in some of the newer processes and phenomena of metallurgy, as shown in the methods adopted to the harnessing of molecular attractions which reside upon the surfaces of solids to the purposes of ore concentration. These methods, which have, for example, completely changed the economic outlook of the great Broken Hill deposits of silver-lead-zinc ores, are there used to separate the blende constituent in saleable form from the "tailings" left behind, after the bulk of the lead and silver have been recovered. But they are applicable in general to all sulphide ores, as well as to finely divided metals and non-metals, such as gold, graphite, carbon, diamond, sulphur, and so on, and they are frequently spoken of as "oil processes," from the fact that in several of them oil is used in larger or smaller quantities, usually in smaller. In such processes there are no chemical reactions to speak of; physical forces of previously unsuspected range and power, so far as commercial applications are concerned, have been induced to do the work more easily, and much more economically, the force mainly concerned being what is called "surface energy."

Equally new, and probably of great importance to the metallurgist of the future, are the developments in colloidal chemistry. The plasticity of clays and "ultra-sliminess" of "slimes" are due to this class of bodies in which inorganic materials ape the reactions of organic; a clay colloid may almost be said to masquerade as a fatty acid.

Mr. Sulman also referred to the extended application of improved magnetic and electrostatic methods for the separation of dry ores, and to catalytic processes of metallurgical importance.

In addressing the prize-winners in conclusion, Mr. Sulman said that to some the occasion might mark a period only in their studies, whilst to others it may mean the termination of their special courses, and that they would now return to the world of practical work and

achievement armed with the mental weapons, the intellectual picks and shovels which had been forged for them in this Institute, and in the use of which they had been rendered proficient. Some of them might presently be called upon to attack the boulders and rocks of tough new facts, and would possibly, and indeed probably, find that the present keen edge of some of these implements would become dull and dented and hacked. The pick of hypothesis and the shovel of theory might, perhaps, break in their hands, but he trusted that they would be in no wise dismayed, but would learn to recognise that theories are, after all, but the temporary instruments of research, continually wearing out and being replaced by others. Such being the case, their work was to forge fresh theories for themselves, better calculated as to shaft and edge, and thus to fulfil their measure of the ever harder work which humanity is called upon unceasingly to achieve.

NOTICES OF BOOKS.

Physical and Chemical Constants and some Mathematical Functions. By G. W. KAYE, B.A. (Cantab.), D.Sc. (Lond.), A.R.C.Sc. (Lond.), and T. H. LABY, B.A. (Cantab.). London: Longmans, Green, and Co. (4s. 6d. net).

THIS valuable collection of Chemical and Physical Constants meets a long felt want. Although moderate both in size and price a surprising amount of valuable information has been collected together and set out in a way that admits of rapid reference. The scope of the work includes General Physics and Astronomy, Heat, Sound, Light, Electricity, Magnetism, Radio-activity, Chemistry, and Mathematical Tables. In some of the sections a brief *résumé* is given, containing references to such books and original papers as are likely to be of interest. The twelve pages devoted to Ionisation and Radio-activity are especially valuable; it is probably the first time that any attempt has been made to collect such data, and this part of the work will be of very great value to those working upon the subject. The book is convenient in size and thoroughly well indexed, and is just one of those books that once acquired it is difficult to realise how one has been able to get along without it.

Subject List of Works on Chemistry in the Library of the Patent Office. Subject List of Works on Chemical Technology in the Library of the Patent Office. London: The Patent Office. 1911. (6d. each).

THE new series of catalogues to the works in the library of the Patent Office represents an improvement upon the old lists in that, besides full titles, dates, and sizes, information is given as to the exact position in the library shelves in which each book is to be found. The books are arranged in chronological order under specific headings, and in addition a full key to the classification of headings is provided, so that readers should have no difficulty in finding with the aid of the guide all the information on any given subject which is to be procured from the library.

Physical Society's Annual Exhibition.—This exhibition, which is to be held on Tuesday, the 19th inst., at the Imperial College of Science, South Kensington, will be open in both the afternoon (from 3 to 6 p.m.) and in the evening (from 7 to 10 p.m.). Prof. the Hon. R. J. Strutt, F.R.S., will give a discourse at 4.30, and again at 8 p.m., on "Electric Discharge and the Luminosity which Survives it." Some thirty firms will be exhibiting. We understand that invitations have been given to the Institution of Electrical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission in all cases will be by ticket only, and therefore Members of the Societies just mentioned (including also the Physical Society) desiring to attend the Exhibition should apply to the Secretary of the Society to which they belong.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 17, October 23, 1911.

Industrial Manufacture of Pure Nitrogen.—Georges Claude.—In Linde's process for freeing the nitrogen of the air from oxygen air is liquefied and then evaporated, the vapour, ascending a rectifying tower, is washed by a descending stream of liquid air containing 21 per cent of oxygen, and the oxygen in the vapour is thus retained by the liquid. In this way nitrogen containing only 7 per cent of oxygen can be obtained. If this impure nitrogen is compressed to about 4 to 5 atmospheres, dried, and then again liquefied and treated as before, a liquid much less rich in oxygen is obtained, and if a reflex condensing apparatus is used 99.6 per cent pure nitrogen can be prepared by progressive condensation and rectification.

Synthesis of New Hydroaromatic Ketones.—G. Darzens and H. Rost.—Hydroaromatic ketones can readily be prepared by the action of an organo-magnesium derivative upon an acid chloride, made by the action of SOCl_2 upon the acid. Thus the chloride of tetrahydrobenzoic acid when treated with the magnesium derivative of hexabrombenzene, $\text{C}_6\text{H}_{11}\text{Br}_6$, yields hexahydrobenzoylcyclohexane, $\text{C}_6\text{H}_{11}\text{CO}-\text{C}_6\text{H}_9$. Similarly the authors have obtained *n*-butylcyclohexane, $\text{C}_6\text{H}_{11}\text{CO}-\text{C}_4\text{H}_9$. Hydroaromatic ketones can be obtained by the same method from the tetra- and hexahydrophenylacetic acids.

Atti della Reale Accademia dei Lincei.

Vol. xx., (II.), No. 7, 1911.

Basicity of Organic Acids containing Alcoholic Hydroxyls.—G. Calcagni and L. Bernardini.—The curves of neutralisation of malic, tartaric, and citric acids obtained by titration with caustic potash, using phenolphthalein as indicator, have as many points of inflexion as there are carboxyls in the molecule. They pass through a minimum, and then rise suddenly and rapidly to the point of complete neutralisation. Beyond this point the curves are parallel to the *x*-axis. The results so far obtained are not conclusive as to the function of the alcoholic hydroxyl in the oxy-acids, since the formation of a salt can neither be proved nor disproved.

Action of Aldehydes on Pyrrol Derivatives.—U. Colacicchi.—The author has prepared the following compounds of aldehydes and pyrrols by the direct union of the constituents:—Formaldehyde and 2.4-dimethyl-3-acetyl, 2.4-dimethyl-5-acetyl, 2.4-dimethyl-5-benzoyl-pyrrol, paraldehyde with the same pyrrols; butyl, isobutyl, and heptyl aldehydes with 2.4-dimethyl-5-benzoyl-pyrrol. These derivatives are characterised by having a high melting-point, which decreases as the weight of the aldehyde increases; they are further characterised by a yellow colour and by their solubility in concentrated acids.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Miss Goldsmid, Dr. Habibur Rahman Khan, Dr. W. M. Noott, and Mrs. Middleton Robinson were elected Members. Prof. W. C. Brögger (Christiana), Geh. Rath Prof. T. Curtius (Berlin), Prof. P. A. Guye (Geneva), and Geh. Regierung Rath Prof. H. Rubens (Berlin) were elected Honorary Members of the Royal Institution. The

Special Thanks of the Members were returned to Mr. D. J. Blaikley for presenting to the Institution, from the bequest of the late Miss J. Barnard and at her express wish, a large volume of Faraday's, containing Engravings, Portraits, and Letters. The Chairman announced that the Managers at their Meeting held this day, had appointed Mr. W. Bateson, M.D., F.R.S., Fullerton Professor of Physiology for a term of three years.

Titanium.—Arthur Stähler and Fritz Bachran.—Titanium trichloride can be obtained by passing a current of hydrogen and titanium tetrachloride vapour through a silundum tube, heated to about 1100° . When the trichloride is heated to $660-700^\circ$ in a current of hydrogen in absence of air it is converted into the dichloride and tetrachloride, $2\text{TiCl}_3 \rightleftharpoons \text{TiCl}_2 + \text{TiCl}_4$. The dichloride can be decomposed into the tetrachloride and titanium by heating to 1100° . The authors have prepared double formates of titanium, and ammonium and potassium respectively by adding solutions of the formate of the metal to a solution of TiCl_3 in absence of air. The double formates give olive-green solutions in water, and are hydrolytically decomposed at 50° , giving dark blue titanium hydroxide and formic acid. The dry salts are comparatively stable in air, but their solutions are readily decomposed. When some drops of an aqueous solution of titanium trichloride are added to a very dilute solution of gold chloride, an intense violet coloration is produced. Colloidal gold is formed, and adsorbs titanous acid. If the violet solution is boiled a voluminous dark blue precipitate separates. It contains both gold and titanium. The dry precipitate is insoluble in ammonia.—*Berichte*, xlv., No. 14.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, before Easter:—Dr. P. Chalmers Mitchell, a Christmas Course of six illustrated lectures on "The Childhood of Animals," adapted to a Juvenile Auditory—(1) Introductory; (2) The Duration of Youth; (3) Colours and Patterns of Young Animals; (4) Young Animals at Home; (5) The Feeding of Young Animals; (6) The Play of Young Animals. Mr. W. Bateson, Fullerton Professor of Physiology, R.I., six lectures on "The Study of Genetics." Prof. E. G. Coker, six lectures on "Optical Determination of Stress and some Applications to Engineering Problems." Dr. T. Rice Holmes, three lectures on "Ancient Britain." Prof. A. W. Bickerton, two lectures on "The New Astronomy." Prof. A. M. Worthington, two experimentally illustrated lectures on "The Phenomena of Splashes." Mr. M. H. Spielmann, two lectures on "The Portraiture of Shakespeare." Mr. F. A. Dixey, two lectures on "Dimorphism in Butterflies—(1) Seasonal Dimorphism; (2) Sexual Dimorphism." The Rev. John Roscoe, two lectures on "The Banyoro—a Pastoral People of Uganda—(1) The Milk Customs; (2) Birth and Death Customs." Sir Alexander C. Mackenzie, three lectures on—(1) "Russian Music of To-day" (with the kind assistance of the Hans Wessely Quartet); (2) and 3) "Franz List (Centenary)," with Musical Illustrations. Prof. Sir J. J. Thomson, Professor of Natural Philosophy, R.I., six lectures on "Molecular Physics." The Friday Evening Meetings will commence on January 19, when Prof. Sir James Dewar will deliver a Discourse on "Heat Problems." Succeeding Discourses will probably be given by Prof. Bertram Hopkinson, Dr. J. Mackenzie Davidson, Dr. J. A. Harker, Rt. Hon. Sir John H. A. MacDonald, Mr. G. K. B. Elphinstone, Dr. W. J. S. Lockyer, Mr. F. Soddy, Prof. D'Arcy W. Thompson, Prof. Sir J. J. Thomson, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Royal Society of Arts, 8. (Cantor Lecture). "The Carbonisation of Coal," by Prof. Vivian B. Lewes.
WEDNESDAY, 13th.—Royal Society of Arts, 8. "Continuous Service in Passenger Transportation," by W. Y. Lewis.
THURSDAY, 14th.—Royal Society of Arts, 4.30. "Fisheries of Bengal," by Dr. J. Travers Jenkins.

THE CHEMICAL NEWS.

VOL. CIV., No. 2716.

DISCOVERY OF A NEW ELEMENT, PROBABLY OF THE PLATINUM GROUP.

By ANDREW GORDON FRENCH.

WELL authenticated reports from Western Canada state that Mr. Andrew Gordon French, a native of Glasgow, and well known as a metallurgist, has discovered in the Nelson district of British Columbia an absolutely new element, which is expected to prove of high commercial value. The new element, it is added, has been named "Canadium" in honour of the Dominion. It is, Mr. French states, of the platinum group, and will probably fill one or other of the two vacant spaces among the noble metals in what chemists know as "the periodic table." These spaces are between osmium and tungsten, and between ruthenium and molybdenum, and it is considered likely that "Canadium" will take its place between the second two.

"Canadium" is of a beautiful white colour, and of brilliant lustre, apparently suitable for gem settings and similar purposes. It was found in the dyke rocks in the Nelson district, running in quantities from a few penny-weights up to three ounces to the ton. It occurs pure in semi-crystalline grains, and in short rods about half a millimetre in length by one-tenth of a millimetre in thickness. Mr. French also found it in metallic particles in the form of scales in platinum-bearing ores. These particles, which have a bluish white colour, contain the metal alloyed with a volatile substance which may be osmium, as it was dispelled by the blowpipe flame, leaving a brilliant bead of "Canadium."

It is not platinum, ruthenium, palladium, nor osmium. It is much softer than these, and is quite easily melted by the blowpipe.

The new metal does not become tarnished by lengthened exposure to damp, and is not oxidised by continued heating in the blowpipe oxidising flame. It is soluble in nitric and hydrochloric acids, and in aqua regia without residue, and its solution in nitric acid yields no precipitate with chloride of sodium solution. This differentiates it from silver. It is not blackened by lengthened exposure to moist sulphuretted hydrogen or to alkaline sulphides, tests which also prove that it is not silver. It is not blackened by tincture of iodine, and its nitrate solution is not precipitated by iodide of potassium. These negative qualities, Mr. French states, differentiate it from palladium.

Its melting-point is somewhat lower than fine gold and silver, and very much lower than that of palladium. It is electro-negative to silver in dilute acid solution. These characteristics definitely show it to be a new metal of the palladium group.

The new element was found in a platinum mine previously discovered by Mr. French, and from which platinum, iridium, palladium, rhodium, and osmium have been obtained.

The above is reprinted from the *Glasgow Herald* of December 5th.

Previous to leaving this country, over twenty years ago, Mr. French was associated with various firms of bullion smelters, and was for many years practically engaged in the extraction and separation of the metals of the platinum group, with all of which he is intimately acquainted.

Mr. Thomas French, son of Mr. Andrew Gordon French, discoverer of the new element, has favoured us with a copy

of a letter he has received from his father, and permits us to publish the following extracts from it:—

Nelson, B.C., Nov. 12th, 1911.

"You will be pleased and may be surprised to learn that I have discovered and isolated a new metal of the platinum group—a 'Noble Metal.' I have been following it up since May last. It is a beauty—certainly the whitest and most lustrous of all the white metals—not tarnished by exposure to damp air, not discoloured by H_2S nor by alkaline sulphides, not blackened by tincture of iodine. These tests differentiate it from silver and palladium.

"It melts at about the same temperature as fine silver. It is electro-negative to silver, and its nitric acid solution gives no precipitate with HCl or NaCl . It is not precipitated by KI . These tests also distinguish it from silver and palladium. It is not platinum, ruthenium, nor osmium, being softer than these and quite easily melted by the blowpipe. In the blowpipe oxidising flame it melts to a brilliant white bead, and does not oxidise after prolonged exposure. But some specimens give off dense fumes for a short time, which may be osmium, or perhaps something also new. After these fumes are gone no further action takes place, and the bead remains unaltered by prolonged heat.

"It is soluble in nitric acid without residue, and soluble in hydrochloric acid and aqua-regia without residue.

"Its alloy with gold and silver in 'parting' proportions is acted on by cold dilute nitric acid as follows:—The silver is first dissolved out, and then the new element, leaving the 'brown gold' in the usual form, but if the action of the acid is stopped when the silver is all dissolved, and the dark residue is then dried and pressed by the blade of a clean polished knife, the colour is a most beautiful and brilliant white. The new metal may then be dissolved out by more exposure to nitric acid and precipitated by zinc. The precipitate may be collected off the zinc and cupelled with lead to a white bead which is not affected by prolonged submersion in alkaline sulphides. The dissolved out silver by the first acid may be precipitated by NaCl , and then cupelled to a white bead which, when dipped into alkaline sulphide, is instantly blackened.

"I am preparing to extract in quantity, and will then examine it for its other reactions and, as far as my opportunities will allow, for its physical properties.

"In the meantime I have lodged a specimen and a provisional description in the Royal Bank of Canada here in Nelson to safeguard me against any public anticipation, and shown it to three friends, the banker, and my two partners, in some of the igneous dykes which produce it, and later on I purpose to send a specimen to the Royal Society in England formally announcing the discovery.

"I have named it 'Canadium' in honour of the country where it has been found. It occurs along with platinum, palladium, and the other platinum metals in metallic grains and scales in igneous dykes in granite country.

"It occurs in the stone, from a few grains to as high as 3 ozs. per ton. It will push out palladium for search light mirrors, as it is more brilliant and easier to work, and it will do well for setting of diamonds, &c., in jewellery."

Catalytic Etherification of Dibasic Acids.—J. B. Senderens and J. Aboulenc.—Malonic acid can be etherified by monatomic alcohols, ROH , according to the equation $\text{CO}_2\text{H}-\text{CH}_2-\text{CO}_2\text{H} + 2\text{ROH} = \text{RCO}_2-\text{CH}_2-\text{CO}_2\text{R} + 2\text{H}_2\text{O}$ in presence of sulphuric acid, anhydrous sulphate of aluminium, or potassium bisulphate. This method of preparing malonic ethers is more advantageous the higher the molecular weight of the alcohol used. Succinic and oxalic acids give similar results. Strictly speaking, there is no catalytic action in the case of orthophthallic acid. To etherify it it is necessary to employ 15 per cent sulphuric acid, when, after an hour's boiling, two layers are formed—a lower aqueous layer and an upper layer containing neutral phthallic ether.—*Compt. Rend.*, cliii., No. 19.

ON THE QUALITATIVE DETECTION
OF CERTAIN ELEMENTS WHICH FORM
INSOLUBLE SULPHATES:
BARIUM, STRONTIUM, (CALCIUM), AND LEAD.
By PHILIP E. BROWNING and PHILIP L. BLUMENTHAL.

IN the ordinary processes of qualitative analysis the alkali earth elements are usually separated by ammonium carbonate, after hydrogen sulphide and ammonium hydroxide have been used to remove the greater number of the bases. It has long been observed by those employing these processes that a considerable part of the alkali earth, especially barium and strontium, fails to appear when the ammonium carbonate is added. The reasons given for this loss have been the oxidation of hydrogen sulphide or other sulphides to sulphates, and the consequent precipitation of the alkali earth sulphates, the formation in alkaline solution of carbonates and the consequent precipitation of the carbonates, and the tendency of the large amounts of ammonium salts which collect during the analysis to interfere with the precipitation of the alkali earth carbonates by ammonium carbonate. Various precautions have been suggested to avoid these sources of error, such as the prompt removal of the excess of hydrogen sulphide by boiling, the use of freshly-prepared hydroxides free from carbonate, and the removal of the ammonium salts by ignition before attempting to precipitate the alkali earth carbonates.

The work to be described in this paper was undertaken to study, first, the effect of a direct precipitation of the insoluble alkali earth sulphates, after the removal of the mercury in the mercurous condition, silver, and the proportion of lead which may be precipitated by hydrochloric acid; and, second, the action of ignition with carbon upon these sulphates. For the work solutions were prepared containing to each cubic centimetre 1 mgrm. reckoned as the element.

Preliminary experiments showed that in a volume of 10 cc., 1 mgrm. of Sr, 0.5 mgrm. of Pb, and 0.1 mgrm. of Ba gave distinct precipitates when treated with a few drops of dilute sulphuric acid and allowed to stand a few minutes, and 10 mgrms. of Ca gave a precipitate on standing over night.

The action of ammonium acetate upon the sulphates of barium and lead was tried as follows:—Two solutions containing 0.1 gm. of Pb and 4 grms. of ammonium acetate in 10 cc. of water gave no precipitate when a slight excess of sulphuric acid was added. On addition of more sulphuric acid the lead sulphate tended to precipitate. When ammonium sulphate was substituted for the sulphuric acid no precipitation took place even in the presence of an abundant excess of that reagent. To test the delicacy of the barium precipitation under these conditions, 1 mgrm. of Ba was added to a clear solution containing 0.1 gm. of Pb, 4 grms. of ammonium acetate, and 1 gm. of ammonium sulphate in 10 cc. of water. The barium sulphate was precipitated at once. It is evident from these experiments that barium sulphate in small amounts may be precipitated in the presence of lead salts by ensuring the presence of a sufficient amount of ammonium acetate, and that ammonium sulphate is to be preferred as the precipitant.

In a previous paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, xxxii., 164) we have discussed the application of fusion with carbon to the reduction of the difficultly soluble double sulphates of the cerium earths with the alkali sulphates, and mentioned the fact that this fusion process had been used for the preparation of soluble barium and strontium salts from barite and celestite. It is now our purpose to show the application of this process to the detection of the alkali earths when present as the sulphates.

Several solutions containing 0.5 mgrm. of Ba were treated with sulphuric acid, the barium sulphate after filtration was treated directly on the filter-paper with a

little pure sugar carbon, and the paper containing the sulphate and carbon inserted in a closed glass tube and heated to full redness for a few minutes. After the ignition the mass was extracted by boiling with a little hydrochloric acid, and after filtration the extract was treated with sulphuric acid. In every case the precipitate was distinct, although in a few instances faint. Comparative tests were made by putting equal amounts of barium sulphate through the treatment just described, and through the well-known fusion process with sodium carbonate (fusing, washing with water, and dissolving the carbonates in hydrochloric acid), with possibly a little advantage in the carbonate process so far as concerns the amount of barium shown, but scarcely enough advantage to balance the saving of time in the employment of the carbon ignition method.

As the outcome of this work the following method is suggested:—

About 10 cc. of a solution which may contain mercury in the mercurous condition, silver, lead, barium, strontium, and calcium, besides other elements, is treated with hydrochloric acid in faint excess and the precipitated chlorides are filtered off. To the filtrate are added about 5 grms. of ammonium acetate and a 10 per cent solution of ammonium sulphate to complete precipitation. After gentle warming the alkali earth sulphates are filtered off and washed with a saturated solution of ammonium acetate until the washings give no test for lead by hydrogen sulphide. The filtrate and washings are reserved for treatment by the ordinary course of analysis. To the precipitated sulphates on the paper a small amount of pure sugar carbon is added, the paper is rolled up, and the mass placed either in a porcelain crucible with a cover or in a closed glass tube and heated to full redness for a few minutes. The fused mass is treated with about 5 cc. of 50 per cent acetic acid and warmed, when, if the alkali earth elements are present, an odour of hydrogen sulphide will generally be evident. The extract is thrown upon a filter and the residue washed with about 5 cc. of water. The filtrate containing acid and water is treated with a few drops of a solution of potassium chromate to test for barium. The barium chromate is removed by filtration, and the filtrate boiled with sodium carbonate to precipitate strontium and calcium as the carbonates. If the precipitate of the carbonates is very small, it may be dissolved in hydrochloric acid and tested spectroscopically. If, however, it is not too minute in quantity, it should be dissolved in nitric acid after careful washing, and the strontium and calcium separated by dehydration with amyl alcohol.

The results are given in the table. All tests for strontium and calcium were confirmed by the spectroscope, and in Nos. 4 and 5 strontium was found by the spectroscopic test.

	Pb present. Grm.	Ba present. Grm.	Sr present. Grm.	Ca present. Grm.	
1.	0.0500	0.0500	0.0500	0.0500	Good tests for all.
2.	0.0250	0.0250	0.0250	0.0250	Good tests for Pb, Ba, and Sr; Ca faint.
3.	0.0100	0.0100	0.0100	0.0100	Pb and Ba good; Sr fair; Ca doubtful.
4.	0.0050	0.0050	0.0050	0.0050	Pb and Ba good; Sr fair.
5.	0.0010	0.0010	0.0010	0.0010	Pb good; Ba fair; Sr faint.
6.	0.1000	0.0050	—	—	Pb and Ba good.
7.	0.1000	0.0010	—	—	Pb good; Ba faint.

From these results it would appear that these tests proposed for barium and strontium, effective to at least a milligram. of each element, may with advantage precede the group precipitation by hydrogen sulphide in the ordinary course of qualitative analysis.—*American Journal of Science*, xxxii., 246.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 16th, 1911.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,
in the Chair.

MR. R. W. MERRIMAN was formally admitted a Fellow of the Society.

The PRESIDENT read the following letter:—

Home Office, Whitehall,
July 24th, 1911.

SIR,—I am commanded by the King to convey to you hereby his Majesty's thanks for the Loyal and Dutiful Address of the President, Council, and Fellows of the Chemical Society on the occasion of their Majesties' Coronation.—I am, Sir, Your obedient servant,

(Signed) WINSTON S. CHURCHILL.

To the Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

The PRESIDENT made the following statements:—

(a) An Address had been presented, on behalf of the Society, to the Royal Academy of Sciences of Turin, on the occasion of the centenary commemoration of Amedeo Avogadro:—

THE CHEMICAL SOCIETY.

TO

THE ROYAL ACADEMY OF SCIENCES OF TURIN.

GREETING,

We, the President and Officers, desire on behalf of the Chemical Society to associate ourselves with you in doing honour to the memory of your illustrious compatriot, Amedeo Avogadro.

Of all the pillars upon which the edifice of modern chemistry is supported there is assuredly none more fundamental, excepting the atomic theory, than the famous and illuminating hypothesis formulated one hundred years since by Avogadro. It would be difficult to exaggerate the indebtedness of Chemical Science to the great Italian Physicist, whose inspired fancy penetrated so deeply into the mysteries of the gaseous state of matter that he was able to reveal its ultimate and quantitative structure to the world.

We would take the opportunity of this Centenary Commemoration to congratulate Italy, not only on this magnificent conception of Avogadro, but also on its far-reaching fructification nearly fifty years later through the genius of Stanislao Cannizzaro.

Signed on behalf of the Chemical Society:—

PERCY F. FRANKLAND, President.
ALEXANDER SCOTT, Treasurer.
G. T. MORGAN } Honorary
ARTHUR W. CROSSLEY } Secretaries.
HORACE T. BROWN, Foreign Secretary.

Dated this Twentieth Day of July, One Thousand Nine Hundred and Eleven.

(b) A Committee has been formed with the object of raising funds for the purpose of erecting a memorial to the memory of Jacobus Henricus van't Hoff, who died on March 1st, 1911. It is proposed to erect a statue of van't Hoff in Amsterdam, where he carried out most of his teaching work, and made most of his important discoveries. Further, to found an "International van't Hoff Institution," from the funds of which Institution scientific investigations will be supported.

Subscriptions may be sent to the Treasurer of the Society (Dr. A. Scott).

(c) A communication has been received from Prof. A. Haller stating that it is proposed to raise a memorial to the late Prof. Paul Schützenberger, and inviting sub-

scriptions to the fund, which should be sent to M. Emile Blondel, 2, rue Ampère, Rouen.

Certificates were read for the first time in favour of Messrs. Thomas Sharp Dick, 15, South Street, Greenock, N.B.; Harold Forster Dodson, 6, Lune Street, Saltburn-by-the-Sea; Ernest George Gaul, M.Sc., The College, Holmes Chapel, Cheshire; Herbert Middleton, M.Sc., 7, Howard Street, Horton Lane, Bradford.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Charles Christian Gardthausen, Assistant Curator, Geological Survey, Pretoria; James Hogan Hill, care of Opium Agent, Ghazipur, U.P. India; Gaston Nilié-Martin, S. African Sugar Refineries Ltd., South Coast Junction, Natal; John Ffrid Richardson, Government Quinine Factory, Mungpu, P.O., Sonada, D.H. Railway, India; Alexey Mikhailovich Vassiliev, The University, Kasan, Russia.

Of the following papers, those marked * were read:—

*286. "Chemical Examination of Calabar Beans." By ARTHUR HENRY SALWAY.

In connection with the preparation of a quantity of the alkaloid physostigmine (eserine), the opportunity was taken for a more complete examination of the other constituents of Calabar beans. The physostigmine, $C_{15}H_{21}O_2N_3$, thus obtained melted at $86-87^\circ$, whereas the recorded melting-point of this alkaloid is $105-106^\circ$ which was found to agree with a pure commercial specimen of physostigmine. This discrepancy was proved to be due to the fact that the alkaloid is dimorphous. In addition to the above alkaloid, the following compounds were isolated:—A new alkaloid, *physovenine*, $C_{14}H_{18}O_3N_2$ (m. p. 123°); a new dihydric alcohol, *calabarol*, $C_{23}H_{36}O_4$ (m. p. 245°), which yields a *dibenzoyl* derivative, melting at $195-196^\circ$; trifolanol, $C_{21}H_{36}O_4$; and palmitic, stearic, behenic, oleic, and linolic acids. A considerable amount of sugar was also present, which yielded *d*-phenyl-glucosazone (m. p. 205°). The alkaloid eseramine (m. p. 245°), and the compounds designated as stigmaterol, $C_{30}H_{48}O$, and sitosterol, $C_{27}H_{46}O$, which had previously been isolated from Calabar beans, were also obtained. It was, however, not found possible to confirm the statements respecting the presence in Calabar beans of the alkaloids designated as "eseridine" and "isophysostigmine" respectively.

DISCUSSION.

Dr. VELEY enquired if the author had studied any physiological properties of his purified samples of physostigmine (eserine) or its salts, such as the hydrochloride or hydrobromide. Having regard to the poisonous properties of the Calabar bean, from which the base is obtained, experiments on the effects on isolated muscle or nerve of the constituent base would be of especial importance in medico-legal cases.

Dr. SALWAY stated that the new alkaloid physovenine, $C_{14}H_{18}O_3N_2$, possessed powerful myotic properties, being similar in this respect to physostigmine, but that its physiological action had not been further determined.

*287. "Organic Derivatives of Antimony. Part II. The Orienting Influence of Antimonic Substituents in the Benzene Nucleus." By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

When treated with a mixture of concentrated nitric and sulphuric acids, phenylstibinic acid, diphenylstibinic acid, and triphenylstibine hydroxynitrate yield nitro-derivatives containing one nitro-group in each benzene nucleus present in the molecule. The orientation of these nitro groups with respect to the antimonic radicles was determined by suspending the nitro compounds in dry chloroform, and heating with a mixture of phosphorus pentabromide and bromine at $120-140^\circ$. These reagents bring about the replacement of antimony by bromine, the fission products being 1-bromo-3-nitrobenzene and antimony bromide. The presence of quinquivalent antimony

in the benzene ring determines the introduction of a nitro-group in accordance with the meta-law of substitution.

m-Nitrophenylstibinic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbO}(\text{OH})_2$, *di*-*m*-nitrodiphenylstibinic acid, $(\text{NO}_2\cdot\text{C}_6\text{H}_4)_2\text{SbO}\cdot\text{OH}$, and *tri*-*m*-nitrotriphenylstibinic acid, $(\text{NO}_2\cdot\text{C}_6\text{H}_4)_3\text{Sb}(\text{OH})_2$, are sparingly soluble, yellowish white amorphous compounds, yielding soluble alkali salts. The reduction of the last of these acids leads to the formation of *tri*-*m*-aminotriphenylstibine, $(\text{NH}_2\cdot\text{C}_6\text{H}_4)_3\text{Sb}$.

The prolonged interaction of triphenylstibine and antimony chloride in xylene solution at 240° results in the formation of diphenylstibine chloride and phenylstibine dichloride,—



(compare Hasenbäumer, *Ber.*, 1898, xxxi., 2911; Michaelis and Gunther, *Ber.*, 1911, xlv., 2316).

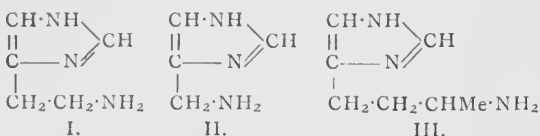
DISCUSSION.

Dr. PYMAN pointed out that Ehrlich and Berthelm (*Ber.*, 1907, xl., 3297) proved the orientation of *p*-aminophenylarsinic acid by converting it into *p*-iodoaniline by boiling with sulphuric acid and potassium iodide, and inquired whether the authors had tried this method on their aminophenylstibinic acids.

Dr. MORGAN replied that the method had been tried, but had proved to be inapplicable in the case of the antimony compounds dealt with.

*288. "Aminoalkylglyoxalines." By FRANK LEE PYMAN.

For comparison of their physiological activity with that of 4(or 5)-*B*-aminoethylglyoxaline (I.), several aminoalkylglyoxalines have been prepared:—



4(or 5)-Aminomethylglyoxaline (II.) was obtained by the oxidation of 2-thiol-4(or 5)-aminomethylglyoxaline with ferric chloride.

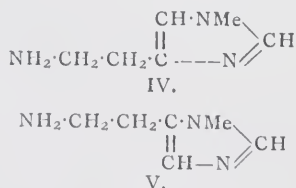
γ -Amino-4(or 5) butylglyoxaline (III.) was formed on the reduction of the oxime of γ -keto-4(or 5)-butylglyoxaline, $\text{C}_5\text{H}_3\text{N}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, a base resulting from the hydrolysis of ethyl 4(or 5)-glyoxalinemethylacetoacetate.

B γ -Bis[4(or 5)-glyoxaline]propylamine,—



resulted from the reduction of $\alpha\beta$ -bis[4(or 5)-glyoxaline]propionitrile.

1-Methyl-4-*B*-aminoethylglyoxaline (IV.) and 1-methyl-5-*B*-aminoethylglyoxaline (V.) were prepared by reducing 1-methyl-4-cyanomethylglyoxaline and 1-methyl-5-cyanomethylglyoxaline respectively, the two isomerides produced by methylating 4(or 5)-cyanomethylglyoxaline:—



289. "The Influence of Neutral Solvents on Velocity of Reaction. Part I. Transformation of Anissynaldoxime in various Solvents." By THOMAS STEWART PATTERSON and HARVEY HUGH MONTGOMERIE.

The influence of various neutral solvents on the rate of transformation of anissynaldoxime in the presence of ethyl tartrate was described, the results being discussed in connection with other work of a similar character.

290. "Copper Salts and their Behaviour with Alkalis." By SPENCER UMFREVILLE PICKERING.

Copper salts of organic acids containing no alcoholic hydroxyl react with alkalis to form insoluble basic salts, whilst those of the oxy-acids form soluble cupri-compounds, either of the *cis*- or *trans*-description; in some cases a certain amount of basic salt is also formed. *trans*-Cupri-salts of monobasic acids are, in nearly every case, very unstable.

Further evidence that copper in cupri-salts is present as CuO , and not as copper displacing hydrogen, was obtained in several cases, especially in that of the salicylate and malate, the latter being of importance, because the compound in question must be of the *cis*-type, and former evidence applied chiefly to compounds of the *trans*-type.

In the case of copper glycerate, a cupri-compound has been obtained, differing in composition from the normal salt only by the elements of water, but certainly not being a mere hydrate. The two compounds have very different solubilities, colours, and decomposition temperatures; and in solution the cupri compound may easily be converted into the normal salt.

Thirteen basic salts precipitated by alkali from salts of acids containing no alcoholic hydroxyl conform to formulæ representing 1, 3, or 7 CuO united with a molecule of the normal salt. Besides these, about twenty new compounds have been obtained.

291. "Contributions to the Chemistry of the Terpenes. Part XII. Synthesis of a Menthadiene from Thymol, and of a Diethylcyclohexadiene from Phenol." By GEORGE GERALD HENDERSON and ROBERT BOYD.

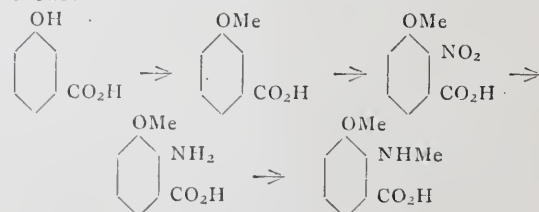
Thymenol (hexahydrothymol), $\text{C}_{10}\text{H}_{19}\cdot\text{OH}$, obtained by hydrogenating thymol according to Sabatier and Senderens' method, when heated with anhydrous oxalic acid, yields as an intermediate product *thymenethyl oxalate*, a crystalline solid, melting at 90° , and finally Δ^3 -menthene, $\text{C}_{10}\text{H}_{18}$. This hydrocarbon unites with bromine to form an oily dibromide, $\text{C}_{10}\text{H}_{18}\text{Br}_2$, which when heated with alcoholic potassium hydroxide yields a menthadiene, $\text{C}_{10}\text{H}_{16}$, probably the Δ^2 :4-isomeride, a liquid which boils at 173 — 174° .

3:5-Diethylphenol, prepared synthetically from phenol, is converted into 1:3-diethylcyclohexan-5-ol, $\text{C}_{10}\text{H}_{19}\cdot\text{OH}$, a liquid boiling at 203 — 205° when heated with hydrogen in presence of nickel. When dehydrated with anhydrous oxalic acid, the latter compound yields 1:3-diethyl- Δ^3 -cyclohexene, $\text{C}_{10}\text{H}_{18}$, a liquid which boils at 163 — 166° , and unites with bromine, forming an oily dibromide, $\text{C}_{10}\text{H}_{18}\text{Br}_2$. On treatment with alcoholic potassium hydroxide, the dibromide yields a 1:3-diethylcyclohexadiene, $\text{C}_{10}\text{H}_{16}$, probably the Δ^3 :5-isomeride, a liquid which boils at 166 — 168° , and resembles in several respects the monocyclic terpenes.

292. "The Synthesis of Damascenic Acid (2-Methyl-amino-3-methoxybenzoic Acid)." (Preliminary Note). By ARTHUR JAMES EWINS.

The alkaloid damascenine is readily converted into the isomeric damascenic acid (Pommerehne, *Arch. Pharm.*, 1900, ccxxxviii., 531). The latter was shown to be 2-methylamino-3-methoxybenzoic acid by Keller, who unsuccessfully attempted its synthesis from methylantranilic acid (*Arch. Pharm.*, 1908, ccxli., 1).

The acid has now been synthesised from *m*-hydroxybenzoic acid by a series of reactions represented as follows:—



Since damascenic acid can be re-converted into the original alkaloid (Keller, *loc. cit.*), the synthesis of the latter is virtually accomplished.

293. "The Oxidation of Camphene with Hydrogen Peroxide." (A Correction). By GEORGE GERALD HENDERSON and MAGGIE MILLEN JEFFS SUTHERLAND.

Geh. Rat Prof. Dr. Bredt has pointed out to the authors what they had unfortunately overlooked, that the name "camphylic acid" which they proposed for the acid $C_{10}H_{16}O_2$ (m. p. 95°), obtained by oxidising camphene with hydrogen peroxide (Henderson and Sutherland, *Trans.*, 1911, xcix., 1539), has already been applied by Perkin to the acid which he prepared by fusing sulpho-camphylic acid with potassium hydroxide. Prof. Aschan has also informed the authors that he has found an acid which apparently is identical with theirs among the products of the oxidation of camphene with potassium permanganate in acetic acid at a low temperature, and he suggests for it the name "camphenic acid." As this name is very appropriate, the authors are glad to adopt the suggestion, and to designate the acid melting at 95° *camphenic* instead of *camphylic* acid.

294. "Note on the Preparation of Labile Benzaldehyde-phenylhydrazones." By FERDINAND BERNARD THOLE.

Thiele and Pickard have shown (*Ber.*, 1898, xxxi., 1250) that ordinary benzaldehydephenylhydrazone is converted into a labile form when its suspension in acetic anhydride is treated with concentrated sulphuric acid and the resulting solution is poured into water. The author has experienced some difficulty in obtaining this product in a crystalline condition, but a good yield of the labile isomeride has been obtained by the method recently described (Dunstan and Thole, *Proc. Chem. Soc.*, xxvii., 233) for the preparation of *syn*-oximes.

Powdered benzaldehydephenylhydrazone is suspended in concentrated hydrochloric acid, and hydrogen chloride passed in to saturation. The resulting red suspension when poured into excess of sodium carbonate gives a bulky yellowish white precipitate of the labile phenylhydrazone. The product crystallises readily from glacial acetic acid, and is evidently identical with that described by Thiele and Pickard (found, N = 14.30; calc., N = 14.29 per cent). It melts at 136°, is very soluble in the ordinary organic solvents, and on repeated crystallisation is slowly transformed into the stable modification (m. p. 152°).

The substance is evidently not identical with the azo-compound, $C_6H_5 \cdot CH_2 \cdot N : N \cdot C_6H_5$, which has been recently described as a yellow oil (*Ann.*, 1910, ccclxxvi., 265).

When the stable modification is moistened with ether and exposed to a current of dry hydrogen chloride, it assumes an orange-red colour, and an increase in weight is obtained approximating to that demanded by the addition of two molecular proportions of hydrogen chloride. Attempts are being made to prepare other labile isomerides by the method described above.

295. "The Separation of Mixtures of Organic Acids by Partial Esterification." By JOHN JOSEPH SUDBOROUGH and EBENEZER REES THOMAS.

The authors are able to show that mixtures of the following types: an $\alpha\beta$ -unsaturated acid and its saturated analogue; an $\alpha\beta$ -unsaturated acid and the $\beta\gamma$ -isomeride; an $\alpha\delta$ -unsaturated acid and the $\gamma\delta$ -isomeride, can be readily separated by partial esterification, using the catalytic method. Under suitable conditions the separation is practically complete after one treatment with alcoholic hydrogen chloride. The method possesses many advantages over Fittig's method of separating mixtures of $\alpha\beta$ - and $\beta\gamma$ -unsaturated acids, more particularly as both acids can be recovered.

296. "Preparation of the Ketones of the Higher Fatty Acids." By THOMAS HILL EASTERFIELD and CLARA MILLICENT TAYLOR.

The authors find that the ketones of the saturated higher fatty acids are very conveniently prepared by

heating the acids with about one tenth their weight of cast-iron turnings to a temperature of about 360°. The method gives good results with the acids from lauric to melissic. Stearic acid gives an 80 per cent yield of stearone.

The unsaturated acids oleic, elaidic, and brassidic also yield ketones, when heated with metallic iron, but the yield is not so good as in the case of the saturated acids. Oleone was shown to be present in commercial "distillation" oleic acid. The method does not give satisfactory results with acetic, butyric, phenylacetic, benzoic, suberic, or sebacic acids.

The following new compounds were described:—*Diheptadecylcarbinol*, m. p. 89.5°, and its *acetate*, m. p. 56.61°. *Cerotoncoxime*, m. p. 78°. *Dipentacosylcarbinol*, m. p. 95°, and its *acetate*, m. p. 58–60°. *Montanone*, $C_{55}H_{110}O$, m. p. 97°, and its *oxime*, m. p. 82.5°. The corresponding secondary alcohol, $C_{55}H_{112}O$, m. p. 101°, and its *acetate*, m. p. 66°. *Melissone*, m. p. 99.5°, and its *oxime*, m. p. 84°. *Oleone*, $C_{55}H_{106}O$, m. p. 59°, and its *oxime*, m. p. 31°. *Elaidone*, m. p. 70°, and its *oxime*, m. p. 32°. *Brassidone*, m. p. 80°, and its *oxime*, m. p. 51°. The ketone of erucic acid was not obtained in a pure state.

297. "Complex Thio-oxalates." By CHARLES STANLEY ROBINSON and HUMPHREY OWEN JONES.

In a former paper (Jones and Tasker, *Trans.*, 1909, xcv., 1904) it was shown that solutions of potassium dithio-oxalate gave an intense magenta colour with a solution of a nickel salt and an intense brown with a cobalt salt; these colours were still visible in solutions containing 1 part of the metal in 40,000,000 parts of water. The behaviour of these solutions indicated the presence of a complex salt, and the authors have now prepared several of these complex salts and others containing palladium or rhodium.

The salts derived from nickel, palladium, and iron have the general formula $M''(COS)_4M'_2$. Potassium, sodium, ammonium, barium, lead, aniline, and phenyltrimethyl-ammonium salts of nickelo-dithio-oxalic acid have been prepared. The molecular weights in solution and the electrical conductivities show that these salts are derived from a dibasic acid.

The salts containing cobalt or rhodium correspond with the formula $M'''(COS)_6M'_3$; determinations of molecular weight and electrical conductivities show that these are derived from a tribasic acid.

Aqueous solutions of nickelo-dithio-oxalic acid have been prepared, and have nearly the same conductivity as equivalent solutions of sulphuric acid, so that this acid is about as strong as sulphuric acid. These solutions decompose gradually on keeping.

298. "The Absorption Spectra of various Iodine Derivatives of Benzene and Toluene as Vapours, in Solution and in Thin Films." By JOHN EDWARD PURVIS.

The results proved that, in the ultra-violet regions, neither the vapours nor the alcoholic solutions, nor the thin films of iodobenzene, *o*- and *m*-iodotoluene, and *o*- and *m*-diiodobenzene exhibited any bands of selective absorption, which had been found previously in the corresponding chlorine and bromine compounds under similar physical conditions, although the number of bands in the latter compounds is decreased as the weight and type of the substituted atom or group of atoms is increased. The phenomena were discussed from a consideration of the heavier iodine atom still further damping and dislocating the vibrations, so that the rhythmical oscillations or vibrations are destroyed, and no selective absorption is possible.

299. "The Transformation of Ammonium Cyanate into Carbamide." By FREDERICK DANIEL CHATTAWAY.

The course of the reaction which takes place when ammonium cyanate is transformed into carbamide has never been satisfactorily explained.

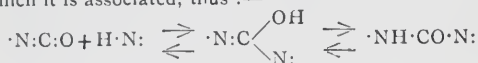
Up to a few years ago it was universally regarded as a

peculiar case of isomeric change, and no consideration was given to the process by which the conversion is effected.

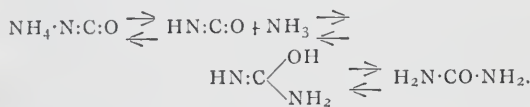
A review of the evidence leads to the conclusion that the explanation put forward by Walker and his co-workers is not correct, and that in the transformation, ammonium and cyanic ions play directly no part.

The change of non-electrolytically dissociated ammonium cyanate into carbamide appears to be a simple process only until the atomic re-adjustments consequent upon it are considered. It is then seen that if it is to be regarded as an intramolecular re-arrangement, it is altogether unusual and exceptional.

The production of carbamide from ammonium cyanate and a large number of other reactions of allied compounds can be brought into harmony if they are regarded as instances of the well known tendency of the carbonyl group to combine with groups such as R_2NH or $R\cdot OH$, followed by subsequent atomic re-arrangements involving only the transference of a hydrogen atom from an oxygen atom to a nitrogen atom, doubly linked to the carbon atom with which it is associated, thus:—



The conversion of ammonium cyanate into carbamide should therefore be formulated as follows:—



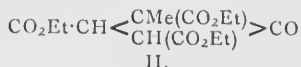
What has hitherto been regarded as the oldest and best known example of isomeric change, is therefore not a case change is therefore not a case of isomeric change at all, but a reaction between cyanic acid and ammonia exactly analogous to the reactions between isocyanic esters and ammonia or amines, whereby substituted carbamides are formed.

300. "The Condensation of Ethyl Citraconate with Ethyl Sodiomalonate. Formation of cyclopentanone-4-carboxylic Acid." (Preliminary Note). By EDWARD HOPE.

This condensation has been previously examined by several investigators with widely differing results (Michael, *Journ. Prakt. Chem.*, 1887, [2], xxxv., 351; Auwers, Köbner, and v. Meyenburg, *Ber.*, 1891, xxiv., 2893; Michael and Schulthess, *Journ. Prakt. Chem.*, 1892, [2], xlv., 57; Ruhemann and Cunningham, *Trans.*, 1898, lxxiii., 1010; Michael, *Ber.*, 1900, xxxiii., 3757). As was first pointed out by Michael (*Ber.*, 1900, xxxiii., 3757), the solvent employed has an extraordinary influence on the course of the interaction. In ethereal solution, condensation occurs, according to Michael, in the normal manner, with the production of ethyl β -methylpropane- $\alpha\beta\gamma$ -tetracarboxylate (I.), but in alcoholic solution the cyclobutane derivative (II.) is supposed to be produced:—

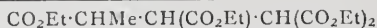


I.



II.

The importance of such a simple method for synthesising cyclobutane derivatives led the present author to examine the reaction more closely with the object, if possible, of extending its application. It was found, however, that the above assumptions regarding the course of the reaction were erroneous. In ether or benzene solution, ethyl citraconate, and the sodium derivative of ethyl malonate yield ethylbutane- $\alpha\beta\gamma$ -tetracarboxylate (III.), because on hydrolysis this ester (III.) gives a mixture of the well-known stereoisomeric butane- $\alpha\beta\gamma$ -tricarboxylic acids (m. p. 186° and 148–152° respectively).

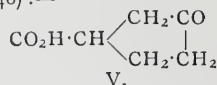


III.



IV.

In alcoholic solution the nature of the product depends on the temperature at which the reaction is conducted. At the ordinary temperature the main product is ethyl butane- $\alpha\beta\delta$ -tetracarboxylate (IV.), probably produced by the isomerisation of ethyl citraconate to ethyl itaconate, followed by the condensation of the latter with ethyl sodiomalonate in the normal manner. At the temperature of the steam-bath, however, the ethyl butane- $\alpha\alpha\beta\delta$ -tetracarboxylate first produced undergoes internal condensation, with the formation of a cyclopentane derivative. From the product of the reaction a keto-acid was obtained (m. p. 60–62°), which gave a semicarbazone m. p. 196–198°, and an oxime (m. p. 177–179°). (The m. p. of this oxime is erroneously given by Kay and Perkin as 141°, instead of 177–179°). This acid was compared directly, and found to be identical with the cyclopentanone-4-carboxylic acid (V.) described by Kay and Perkin (*Trans.*, 1906, lxxxix., 1646):—



V.

It seems clear that the substance (I.) is not formed in the above condensation, because the author has been unable to isolate even traces of β -methyltricarballic acid from the products of hydrolysis, and, indeed, this acid, which the author hopes to prepare, is at present unknown.

The author is also engaged in the further investigation of the mechanism of the formation of cyclic substances in reactions similar to that represented above.

301. "The Relative Activities of certain Organic Iodo-compounds." (Preliminary Note). By DAVID SEGALIER.

The reactivities of some alkyl iodides with sodium phenoxide in alcoholic solution have been measured. The author finds in this reaction a normal decrease of the velocity constant with increase in molecular weight. The following iodides have been investigated:—Methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *tert.*-butyl, isoamyl, *tert.*-amyl, hexyl. An abnormal result is obtained in the case of isopropyl iodide. Measurements are being made at various temperatures, and the investigation is being extended to other iodides and iodo derivatives.

(To be continued)

PHYSICAL SOCIETY.

Ordinary Meeting, November 24th, 1911.

A PAPER on "The Maximum Value of the Electric Stress between Two Unequal Spherical Electrodes," was read by Dr. A. RUSSELL.

The experiments carried out by F. W. Peek (*Journ. Am. Inst. of Electrical Engineers*, 1911) for the General Electric Company of America prove conclusively the value in practical work of a knowledge of how to compute the maximum value of the electric stress between high-pressure conductors. With equal spherical electrodes the electric stress between them can easily be computed from known tables. When, however, they are unequal the calculation becomes so laborious that it is prohibitive to nearly every experimenter. The author develops formulæ for this case, by means of which, and of the formulæ for the capacity coefficients given in a recent paper to the Society, the calculation is very appreciably shortened. When the distance between the spheres is very small compared with the diameter of either, the following approximate formula

for $R_{\max}$. (the maximum value of the electric stress) can be used—

$$R_{\max.} = (V/x) \left[1 + \frac{(2b-a)x}{(3ab)} + \frac{1}{4} \left\{ \frac{(a-b)^2}{ab} + \frac{x^2}{(45a^2b^2)} \right\} \right],$$

where V is the maximum P.D. between the electrodes, x their distance apart, a the radius of the smaller and b the radius of the larger sphere. In this case a knowledge of the values of the capacity coefficients is not required.

Mr. E. H. RAYNER stated that the value of $R_{\max}$. found by the General Electric Co. was 10 per cent lower than that given by some experiments of his own.

Prof. C. H. LEES said that experimentalists must try and verify Dr. Russell's formula, and asked whether the presence of ions between the spheres would alter the value of $R_{\max}$. appreciably.

Dr. R. S. WILLOWS asked how the maximum stress found by Dr. Russell agreed with the stress required to produce ions. He further pointed out that the sparking potentials are different according as to whether the small sphere is positive or negative.

Mr. APPEYARD pointed out the simplification of the formula when the two spheres are equal.

Mr. W. DUDELL observed that now that continuous current at from 50,000 to 100,000 volts, with plenty of power behind it, was available in London further experiments on sparking potentials should be made.

The AUTHOR, in reply, stated that he had read Mr. Peek's paper, and that his results agreed with Poynting's ionic experiments to 2 or 3 per cent. With a small Wims-hurst machine there was a difference of 3 or 4 per cent in the sparking potential, according to whether the small sphere was positive or negative. When the small sphere was positive the electric strength of the air was weaker. This difference, he thought, would disappear if there were more power available.

A paper on "*The Cubical Expansion of Fused Silica*" was read by Mr. F. J. HARLOW.

The author describes experiments in which measurements of the cubical coefficient of expansion of fused silica from 0° C. to 100° C., and from 0° C. to 184° C., were made by the weight thermometer method. The values obtained were $\alpha_{SiO_2} = 99.8 \times 10^{-6}$, and $\alpha_{SiO_2} = 144.7 \times 10^{-6}$. The fundamental coefficient is considerably less than that calculated from previous linear measurements, whereas α_{SiO_2} is only slightly less. A low value of the fundamental coefficient is to be expected, since the coefficient has been shown to change sign at about -80° C. Observations of the ice-point before and after heating showed that no permanent change in the volume of the bulb occurred through heating, thus confirming the utility of fused silica for thermometric purposes.

Dr. G. W. C. KAYE said that the above results should be useful now that mercury in silica thermometers are an accomplished fact and bid fair to revolutionise mercurial thermometry. He pointed out that Mr. Harlow's results did not agree with the linear expansion found by Chappuis, Holborn and Henning, or Randall and Scheel. Some preliminary results on a silica meter bar at the National Physical Laboratory confirmed these other workers.

The PRESIDENT remarked that he had found that the expansion of silica was practically linear with no peculiarities up to 1400° C., though there might be some below 0° C. He pointed out that the cubical expansion may not be three times the linear, since silica cannot be perfectly annealed. If kept at 900° C. for a considerable time it devitrifies.

The AUTHOR, in reply, said it was quite possible the cubical expansion could not be deduced from the linear. He was endeavouring to extend his results to a higher temperature.

A paper "*On the Temperature Coefficient of Diffusion*" was read by Mr. B. W. CLACK.

The paper describes further experiments carried out by the author with an improved form of the apparatus pre-

viously described (*Proc. Phys. Soc.*, xxi., 374, by means of which the value of the coefficient of diffusion of salts through water can be found at various temperatures).

Special flasks, similar to those already employed, were filled with the solution under investigation, and one was suspended from each arm of the balance in a large bath of distilled water maintained at constant temperatures in a thermostat room. The diffusion tubes of both flasks were of equal length, but their cross sections differed considerably, and a method of differential weighing was used to compensate for any small changes in temperature.

From the rate at which the flasks change in weight the value of the coefficient of diffusion of the salts is deduced. Figures are given for this value in the case of KCl and KNO₃ at various concentrations and at different temperatures, and from these figures the temperature coefficient of diffusion is found.

Dr. GRIFFITHS remarked that the time taken to attain a steady state could be reduced to one-ninth by filling the tube for two-thirds of its length with a solution of two-thirds strength, and filling the remaining third with water, and suggested the use of several narrow tubes instead of one wide one. He also suggested the liquids should be sterilised.

Prof. C. H. LEES said that Dr. Griffiths' suggestion of using several narrow tubes was important. We were much in need of further experimental data regarding diffusion.

Dr. H. BORNS asked whether the apparatus consisted entirely of glass.

The AUTHOR, in reply, attached great importance to Dr. Griffiths' suggestion. The apparatus was almost entirely made of glass.

A paper on "*The α -Particles Emitted by the Active Deposits of Thorium and Actinium*," by Messrs. E. MARSDEN and T. BARRATT, was read by Mr. T. BARRATT.

In a previous paper (*Proc. Phys. Soc.*, Aug., 1911) the authors showed that if α -particles are counted on a zinc sulphide screen at a mean rate of μ per second, then the probability of occurrence of a time interval, of length between t and $t + \delta t$, is $\mu e^{-\mu t}$. This formula may be applied to test whether two α -particles are given off simultaneously from a disintegrating atom or whether in any source of α -particles there exist two successive α -ray products, the latter being of short life.

In the previous paper uranium and polonium were shown not to give such irregularities, and in the present paper the same result has been found for actinium and thorium active deposits, although experiments of various investigators pointed to the probability of positive results.

The experiments further suggest a lateral disintegration in thorium active deposit, and this is proved to be the case by results which show that the two α -ray products in Thor. Act. Dep. (ThC₁ and C₂) do not give an equal number of α -particles when the active deposit is in equilibrium, which is required by the ordinary disintegration theory. Thus it is concluded that of the atoms ThC, 35 per cent give rise to α -particles of 4.8 cm. range and 65 per cent to α -particles of 8.5 cm. range, with probably the intermediate emission of β -particles. Various cognate questions are also discussed in the paper.

A paper on "*The Magnetic Transition Temperature of Cementite*," by Messrs. S. W. J. SMITH, W. WHITE, and S. G. BARKER, was taken as read.

The temperature at which cementite (carbide of iron) loses its ferro-magnetism is determined sufficiently accurately for purposes of thermo-magnetic analysis, and examples are given to show the possibility of using the thermo-magnetic properties of cementite to determine whether that substance is present in any iron-carbon alloy.

Prof. S. P. THOMPSON wrote expressing his interest in the problem discussed by the authors, and suggesting that it would be interesting to know whether structurally free cementite differs thermomagnetically from the cementite extracted from pearlite.

The SECRETARY replied that this, amongst other questions, had been considered. The paper contained an account (intentionally very brief) of a few only of the experiments they had made. It was worth remembering that under ordinary circumstances two forms of cementite probably could not exist in equilibrium with iron except at one particular temperature.

INSTITUTE OF CHEMISTRY.

MR. BERTRAM BLOUNT delivered his second lecture on "Cement" at King's College, on Friday, December 1st, Prof. RAPHAEL MELDOLA, F.R.S., Vice-President, occupying the Chair.

Proceeding to the more practical details of his subject, Mr. Blount pointed out that, owing to our limited knowledge of the chemistry of cement, it is necessary to resort to tests of a physical and mechanical nature in order that the user may be able to satisfy himself that the product he employs will meet the demands laid upon it. From their very nature such tests must be arbitrary, and, to ensure uniformity, they must be carried out under standard conditions which will satisfy the requirements of the consumer and not lay too heavy a burden on the producer. Mr. Blount was assisted by Mr. Gillett, who demonstrated the method of mixing the cement to be examined, on which so much of the reliability of the test depends—a point which was illustrated by the story of a firm who undertook to subject a cement to mechanical tests, and reported that a briquette had been made and had been found to contain a large number of voids. Since cement is not deliberately used under tension, it would appear at first sight to be more logical to appraise its mechanical strength by compressive rather than tensile tests; but as all the tests are merely used as a basis for comparison, and the errors inherent in compression tests largely invalidate the results, it has become customary to omit them in favour of tensile tests of either the neat cement or of mixtures of cement and sand of a given degree of fineness. Much prominence has been given to the advantage of testing mixtures of cement and sand, on the ground that such a method approximates more closely to the conditions obtaining in actual practice, whilst, on the other hand, it can equally be urged that the sand prescribed by any standard specification will differ widely both in size and shape from the aggregate usually employed on a commercial scale. For the user of cement the question of soundness, *i.e.*, the property of remaining constant and unalterable in volume, must always be of paramount importance, and justifies the decision of the British Standards Committee in adhering to the simple Le Chatelier test, which has not infrequently been subjected to severe and rather adverse criticisms in some countries. The methods prescribed in the standard specifications of to-day are virtually the same as those laid down some seven years ago, and the quality and uniformity of the modern product have been so well maintained that almost the only alterations have been in the direction of increased stringency, without thereby laying an unreasonable task upon the producer. The information obtained from the ordinary physical and mechanical tests is sufficient for all practical purposes, and probably will not be usefully augmented until some methods are devised for determining the proximate composition of cement and the setting time of concrete. That the former of these has not yet been realised is shown by the fact that, in spite of numerous attempts, no reliable method exists of ascertaining the content of so called "free lime" in cement.

Turning to the economic side of the subject, it was pointed out that mainly through the introduction of the rotary kiln the cost of production of Portland cement had been so far reduced as to render possible the application of the material to uses in which lime had previously held the field; so that at the present time a limit can hardly be set to its sphere of usefulness. It was shown that, whilst

theoretically concrete should weigh about 162 lbs. per cubic foot, the figure found in practice rarely exceeds 140 lbs., or, in other words, about 14 per cent consists of voids—a fact not to be ignored by engineers. (This consideration at once suggests the possibility of increased economy in construction by using every endeavour to make concrete denser and consequently more efficient). Not only may a saving of material be effected thereby, but a further advantage is gained from the fact that the denser product will be less pervious and better able to resist the action of water. It must be borne in mind that water continually exerts a solvent action on cement, and it is obvious that the life of the concrete depends in a large degree on its power of resisting penetration.

For structures of concrete exposed to the action of water, the liberal use of cement is an obvious means of securing imperviousness; but the employment of some substance, *e.g.*, of the pozzolanic class, which will combine with the hydrated lime set free in the process of setting of cement, is perhaps not so common. In the selection of a suitable aggregate not only must its texture be taken into consideration, but also the possibility of any chemical action that it may exert in the concrete; thus debris containing sulphates or easily decomposable silicates is unsuitable. So much has been said of the danger of "magnesia in cement" that the amount allowed has been reduced to quite a low figure. Undoubtedly there has been considerable confusion over this point; the presence of magnesium compounds in structures that have failed under sea-water conditions was really due not to the presence of magnesium compounds in the original cement, but to the formation of magnesium hydroxide by the reaction of the magnesium salts in sea water with the lime compounds of the cement.

After thus outlining a few of the intricate problems that may be presented to the technical adviser, Mr. Blount sketched out a course of training for those who intended to specialise in the subject. After a broad elementary education he insisted on a sound general knowledge of chemistry, supplemented if possible by some mechanical and engineering training, before attempting to proceed to a post-graduate training in the chemistry of cement. This should be gained in a laboratory within easy reach of some centre of the industry where access to works can be obtained, in order that the student may be able to free himself from the small details of laboratory practice and grasp the broad principles, technological and economic, that underlie success in any chemical manufacture.

In conclusion, Mr. Blount briefly reviewed the present position of our knowledge of the chemistry of cement, and paid a high tribute to the valuable results achieved many years ago by Le Chatelier, which remain but slightly modified to-day.

In moving a vote of thanks to the lecturer, and to King's College for the use of the Lecture Theatre, Prof. MELDOLA expressed the opinion that the Institute had made a very good start with the new scheme of lectures, one of the principal objects of which was to bring senior students and young members into personal contact with acknowledged authorities on various subjects, and he mentioned that the lectures would be published.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, December 4th, 1911.

Mr. E. GRANT HOOPER in the Chair.

THE following papers were read and discussed:—

"Physical Properties of Clays." By W. C. HANCOCK.

The ultimate analysis of a clay, although affording useful information on certain points, gives no indication of the working properties. The gap can be filled for some purposes by the "rational analysis" which separates the

material in three mineral constituents, "clay substance," quartz, and felspar. The actual working characters, however, can only be judged from measurements of the physical properties. The tests are made on (a) the raw or unburnt, and (b) the burnt clay, and comprise—

a.	b.
Specific gravity	Specific gravity
Plasticity	—
Shrinkage on drying	Shrinkage on firing
Tensile strength	Tensile strength
Texture (size of grain)	—
	Porosity
	Fusibility

A short description is given of various methods that have been used for measuring these properties, and a few results obtained on clays of different kinds. Certain precautions are necessary; for example, in the case of the shrinkage on drying the amount of water present should be noted, and in the case of the burnt pieces the temperatures.

The practical value of such tests and their bearing on questions of manufacture is indicated.

"Value of the Non-tannins in the Formation of Leather." By Dr. J. GORDON PARKER and J. R. BLOCKEY.

The experiments recorded in this paper were undertaken to determine what influence the non-tanning matters in a tanning material or extract have on the penetration of the tanning matters, or the yield in weight of leather and on the quality of the leather produced. By certain methods of manufacture of extracts, closed autoclaves are used for the extraction of the raw material instead of the open extraction vats. The "pressure extracts" so produced contain a relatively higher amount of non-tanning matters than the extracts produced by open extraction, and it is sometimes claimed that this higher amount of "non-tans" penetrates the fibres of the leather and gives a higher yield of leather. The results of the present experiments show the opposite effect, viz., that the increase in the amount of "non-tans" retards the penetration of the tan, and that the quality of the leather is inferior when an excess of the "non-tans" is present.

In the experiments pieces of pelt were tanned out, both by agitation and suspension, in liquors which were made to contain different amounts of the non-tanning matters but the same amounts of tanning matter. The penetration of the tannin was measured, and the resulting leathers were analysed to determine the effect on the total amount of tannin absorbed and on the quality of the leather. Experiments were made with chestnut and oak-wood extracts, and tannage by drumming and by suspension, and in every case the effect was the same. The excess of "non-tans" retards the penetration of the tannin and yields a poorer leather.

One effect of the increased quantity of "non-tans" is that the liquors, on standing, develop more acidity.

"Estimation of Carbon Monoxide." By L. A. LEVY.

The various industries, &c., in which a rapid and simple quantitative test for carbon monoxide is of value, are mentioned. The use of cuprous chloride absorbents is criticised, and the various attempts which have been made to estimate carbon monoxide colorimetrically, using the reduction of palladium chloride solution or the formation of carboxyhaemoglobin in a dilute solution of blood, are briefly described.

A very dilute solution of gold chloride—originally light yellow—turns red owing to the formation of colloidal gold when carbon monoxide is bubbled through. This reaction was arranged as a colorimetric method of empirically estimating carbon monoxide. The method was not employed to any extent, as the one described subsequently gave complete satisfaction. The gas containing carbon monoxide is drawn through a tube containing iodine pentoxide and copper, maintained at 150–170° C. in an air-bath.

The carbon monoxide is completely oxidised to carbon dioxide, and the gas next passes through an absorbing coil of particular shape, which contains a measured amount of standard baryta solution coloured with phenolphthalein. The solution becomes colourless after the absorption of 20 cc. of carbon dioxide. The volume of gas is equal to that of the water which has run out of the aspirator into a measuring cylinder. If the gas to be analysed contains unsaturated hydrocarbons or carbon dioxide these must be removed by means of suitable absorbents prior to the oxidation of the gas. The measuring cylinder is graduated directly in percentages of carbon monoxide. For the estimation of traces of carbon monoxide a solution of baryta of 1/10th strength is employed. Whether the percentage of carbon monoxide is large or small the colour change is very sudden and readily observed. The results are accurate to within 0.5 per cent of an ordinary Bunte analysis. An arrangement of the complete test in a handy and portable form is described.

"Composition of *Bassia Fats*." By RUSSELL G. PELLY.

The fatty acids of the fats derived from the seed kernels of *Bassia butyracea*, *B. longifolia*, and *B. latifolia* were investigated. The samples of fat were prepared in the laboratory from seed of well authenticated botanical origin forwarded to the Imperial Institute from India.

Bassia butyracea.—The seed kernels contained from 61.2 to 66.9 per cent of fat of a firmer consistence than those of *B. longifolia* or *B. latifolia*, consisting approximately of olein 46 per cent, palmitin 54 per cent.

Bassia longifolia.—The seed kernels contained from 55.3 to 57.8 per cent of fat, consisting approximately of 60 per cent of olein and linolein together, in the proportion of about 6 to 1, and stearin and palmitin together 40 per cent. Traces of volatile acids were also detected.

Bassia latifolia.—The seed kernels contained from 33.0 to 46.0 per cent of fat; the lower figure is probably abnormal owing to immaturity of some of the seed in this sample. The fat is very similar to that of *B. longifolia*, and consists approximately of olein 66 per cent, stearin and palmitin 34 per cent. No linolein could be detected, but further samples will have to be examined before it can be stated definitely that the fat of *B. latifolia* differs from that of *B. longifolia* in this respect.

RÖNTGEN SOCIETY.

At the meeting of the Röntgen Society on December 5th Prof. W. H. BRAGG, F.R.S., of Leeds University, delivered a lecture on "The Energy of the X-Ray," in the course of which he put forward a new theory in radio-physics. He said that the rays, considered in terms of physical science, led to a re-consideration of the rival theories with regard to the nature of light. As they were well aware, one of these theories—the wave theory—supposed ethereal waves of light throughout space, and the other or corpuscular theory, which Newton advocated, supposed light to consist of particles shot out from the illuminating body to the eye. The lecturer did not oppose the wave theory of light, from which he thought no one could escape, but at the same time some of the phenomena of light seemed to fit better into the corpuscular hypothesis than into the other, and this was certainly true of the X-rays. In asking his auditors to regard the X-rays from the point of view which made them appear to be corpuscular, he reminded them that the rays produced ionisation in the air through which they passed, and excited in the material on which they impinged swiftly-moving electrons. When the ions were formed in a gas by the passage of rays, the electrons dropped from the atoms with comparatively small speed, like fruit from a tree which had been struck. But X-rays impinging on a solid substance caused electrons having great speed together with the power of giving rise to phosphorescence. Prof. Bragg carefully examined the view which regarded

the atom as a store-house, the energy being derived from without. He thought this view was untenable. He regarded the X-ray as something which maintained its energy to the end, which did not spread in transmission, and which on striking an atom imparted the whole of its energy to one electron. The function of the atom he considered to be that of the converter, turning the energy of the X-ray into the energy of the electron. Such an idea was permissible on the corpuscular theory. The X-ray did nothing as it went, and the energy which it was conveying so quietly—without, as it were, spilling any of it—was suddenly transformed into electronic energy, and it was the electron within the body, not the X-ray itself, which must be held to account for what were universally spoken of as X-ray effects, beneficial or the reverse. The X-ray was only a carrier of energy along a discrete channel. It might be likened to a shot from a gun, the shot being the carrier of the whole of the energy, and that energy being discretely deposited at one point—the point, namely, where the ray came to an end, being stopped by the solid matter. The critical-point of the whole matter was that, if X-rays and light were the same thing to begin with, why was it that one kind of work was best explained by the ethereal wave hypothesis, and the other by the corpuscular? At present he saw no means of getting over this difficulty. Certainly the γ - and X-rays acted almost like corpuscles moving within a certain limited area.

NOTICES OF BOOKS.

Technical Methods of Chemical Analysis. Edited by GEORGE LUNGE, Ph.D., Dr. Ing. English Translation, Edited by CHARLES ALEXANDER KEANE, D.Sc., Ph.D. Volume II., Parts I. and II. London: Gurney and Jackson. 1911. (£3 3s. net).

THE advance proofs of the new German edition of Lunge's "Technical Methods of Chemical Analysis," Vol. II., were placed in the editor's hands when the English edition was in course of preparation, and thus the improvements and alterations which are to be made have been incorporated in it, as far as they are applicable to English practice. Part I. of Volume II. treats of the metallurgy of iron and other metals, manures, feeding stuffs, explosives, fireworks, acetylene, and carbide, &c., while Part II. is occupied with illuminating gas and ammonia, the coal-tar dyes, and organic dyes. The section on organic dyes has been taken from Volume IV. of the German edition. The book is too well known to need any eulogy, and it must be regarded as an indispensable possession by all technical chemists and analysts.

Die Metallurgie des Wolframs. ("The Metallurgy of Tungsten"). By Dr. HANS MENNICKE. Berlin: M. Krayn. 1911. (15 Mk.).

THE chemistry and technology of tungsten are fully discussed in this book, which is of a most comprehensive type. The author has spared no trouble in compiling his material and arranging it in the most convenient form, and the book is a model of what a practical handbook should be. The treatment of tungsten ores is discussed in full detail, and information relating to cost, yield, and other technical matters is copious and apparently well authenticated. Much attention is paid to the question of the purification of commercial ores and the preparation of the metal, while the physical and chemical properties of the most important compounds and alloys are described. Methods of analysis, on the other hand, are treated only briefly as being outside the scope of the book. Throughout special attention is paid to electrical methods of preparing tungsten, and the author subjects many of the methods he describes to a careful and impartial criticism.

Catalogue of Exhibits of British Chemical Industries Section, Turin Exhibition, 1911. London: Eyre and Spottiswoode, Ltd. (6d.).

THIS book is much more than a mere catalogue of exhibits, and it is quite possible that it might be worth while to bring it to the notice of technical students and chemical manufacturers. It contains many descriptive articles on the positions of some of the principal branches of chemical industry, written by such eminent authorities as Dr. F. Mollwo Perkin, Prof. V. B. Lewes, Dr. Lewkowitsch, Sir Boverton Redwood, and others almost equally well known. These articles are based upon those which were written for the catalogue of the Brussels Exhibition, but have been thoroughly revised, and when necessary amended. An article on the rare elements by Dr. F. M. Perkin has been added.

CORRESPONDENCE.

THE CHANCES OF THE ENGLISH CHEMIST

To the Editor of the Chemical News.

SIR,—I think that it is quite time someone took up the case of the English chemists and their prospects in this country.

It is very seldom you read anything dealing with this question in any of the recognised chemical journals, but it has become a very serious question for chemists to make a living with anything like the ease and comfort they had twenty years ago.

Everyone will agree that to be at least an ordinary chemist in the sense of the word, he must spend innumerable hours of hard and diligent study at the expense of his health and pocket.

No one doubts that such subjects as physics, mathematics, inorganic and organic chemistry, oils and fats, and other specialised branches of the chemical industry, cannot be learnt without the student giving absolutely all his time and the best of his abilities to the study of them.

In short, it is recognised that a chemist must digest some of the most difficult and intricate matters of any science, and yet we have English chemists with all these qualifications earning only 30s. a week. A sum which unskilled labourers are now claiming.

I daresay some will quite agree with this statement, but others will not; but it is a fact, and I think they will all agree, that the English chemist is one of the most underpaid men of any technical trade.

We all are aware of the vast advance in education during the last ten years, but this really does not affect the chemist, who must in all cases be well educated, and the reason why he is so underpaid is accounted for in the following ways:—

Voluntary foreign chemists who will work for a small salary simply to acquire a works experience, and in many cases a knowledge of the English language.

Men fresh from the universities who desire a practical knowledge of the chemical trade, and who will take a situation for a very small remuneration.

These two classes of men are an absolute "drug" on the market, and do more harm to the chances of the ordinary chemist making a living than people can imagine.

I speak from experience, as I have been connected with the chemical trade for a great number of years, and I may mention that it has come to my knowledge of an English chemist at a large tar distillers in this country having a modern plant, and doing a very good business, asking for an increase in salary over 30s. per week, and he was answered as follows:—

"We can get men with university training with two or three letters behind their name for 25s. weekly."

Such is the sort of encouragement given to a chemist to

try and bring new ideas forward, economise, and get the best results at the minimum cost, not forgetting the responsibility for all the products manufactured.

This is a burning question with hundreds of well trained young men in this country, many of whom have brilliant ideas, which are lying dormant through lack of support and interest on the part of their masters.

We must remember that the future of the chemical industry lies on the rising generation of chemists, and we all agree that the principal part of the chemical trade in this country is more or less run on foreign chemists' investigations.

Let our manufacturers, scientists, and other people connected with the trade give their chemists an opportunity, and they, I think, will show that they are at least worth a living wage.

Trusting that you will excuse my trespass of your valuable space, and perhaps some other subscriber will be able to throw some further light on the matter, and how it may be remedied.—I am, &c.,

J. S. MORRISON.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 18, October 30, 1911.

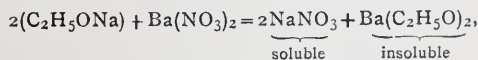
Theory of Solutions and Heats of Solutions.—Albert Colson.—The author has shown that the dissolved particle is generally polymolecular, and has suggested the name "dissolecule" for it. The heat of solution of a gas is equal to its heat of condensation increased by the heat disengaged by the molecular contraction which gives rise to the formation of the dissolecule. The theory of dissolecules agrees with the principle of mechanical equilibrium.

Electrical Properties of Alkaline Metals, Rhodium and Iridium.—MM. Broniewski and Hackspill.—The thermo-electric power of the alkaline metals referred to lead are as follows, the numbers being expressed in microvolts:—

	dE/dt .
Cs	+0.66 -0.0010 <i>t</i>
Rb	-8.26 -0.0302 <i>t</i>
K	-11.33 -0.0376 <i>t</i>
Na	-4.16 -0.0144 <i>t</i>
Rh	+2.17 +0.0005 <i>t</i>
Ir	+2.44 -0.0014 <i>t</i>

The specific resistance of rhodium at 0° is 4.70, and of iridium 6.10.

Use of Liquid Ammonia in Chemical Reactions; Researches on Alcoholates.—E. Chablay.—Barium ethylate can be prepared according to the equation—



if liquid ammonia is used as solvent. An alcohol dissolved in liquid ammonia immediately decolorises a blue solution of sodammonium or potassammonium, $ROH + NH_3Na = RONa + NH_3 + H$. Similarly, an alcohol dissolved in liquid ammonia decolorises a solution of calcium-ammonium, $2ROH + (NH_3)_2Ca = (RO)_2Ca + 4NH_3 + H_2$. This is remarkable, because calcium does not act on alcohols. By using calcium-ammonium the methylate, propylate, and butyrate can be prepared. Barium-ammonium and strontium-ammonium behave like calcium-ammonium.

Oxy-β-methylthiophenes.—M. Lanfry.—When H_2O_2 acts on β-methylthiophene two compounds are obtained, the dioxy derivative, $C_4H_3S.O_2-CH_3$, and the tetroxy derivative, $C_4H_3S.O_4-CH_3$. They are colourless liquids, which become yellow when exposed to the air. They are both insoluble in water, but soluble in all the usual organic solvents. The oxygen in them is united with the sulphur. They give an intense green coloration with isatine, changing to blue on addition of a little water, and disappearing altogether with an excess of water. The tetroxy compound gives with bromine a tetrabromide of tribromotetroxy-β-methylthiophene, $C_4Br_3(Br_4)S.O_4-CH_3$.

No. 19, November 6.

Conditions of Production of Swan Spectrum.—J. Meunier.—The author has shown experimentally that the Swan spectrum is essentially a spectrum of oxidation and explosive combustion. It indicates the presence of oxygen as well as that of hydrocarbons, and hence oxygen must be present in those comets in which the Swan spectrum has been observed.

Radium Emanation in Gases from Springs a Colombières-sur-Orb.—Jacques Danne and Victor Crémieu.—Large quantities of gases are liberated from the springs at Colombières-sur-Orb. They consist principally (about 95 per cent) of carbon dioxide, and also contain considerable quantities of radium emanation. Thus in twenty-four hours 43,000 litres of gas were evolved, the total quantity of emanation being 860 (in mgrm.-minutes).

General Relation between the Physical Properties of Substances.—G. Ter Gazarian.—The author has shown that the following physical properties obey a general law:—Density in the liquid state, coefficient of viscosity, height of capillary ascension, rectilinear diameter of Caillietet and Mathias, and latent heat of vaporisation. The law is—"At temperatures equidistant from the respective critical temperatures, the quotients of the numbers representing each of these properties for any two substances is a linear function of the temperature." In this paper the author gives the data he has obtained by applying this relation to the densities of ammonia, carbon monoxide, benzene, acetic acid, all referred to pentane, and the calculated and observed densities show a remarkably good agreement.

Molecular Refraction of Azo-compounds.—H. Duval.—The solvent appears to have an appreciable influence upon the molecular refraction of azo-compounds. The ortho- and meta-positions of the substituent group give such slight variations that no conclusions can be drawn as to differences in the constitution of the compounds. The molecular refraction increases slightly with the temperature. If Brühl's value is taken for nitrogen the calculated molecular refraction is decidedly lower than the observed value.

Cryoscopy in Fused Sodium Hyposulphite.—A. Boutaric.—The congelation-point of $Na_2S_2O_3 \cdot 5H_2O$ is 48.5°. The equilibrium temperature of the solid salt with 5 molecules of water and that with 2 molecules of water and the solution is 48.2°. The molecular lowering of the freezing-point of urea, glucose, and the salts of sodium in fused sodium hyposulphite is about 44°. The following are the molecular lowerings of some other salts:—

Potassium nitrate	86 (43 × 2)
Ammonium nitrate	82 (41 × 2)
Potassium chloride	83 (41.5 × 2)
Potassium sulphate	122 (40.6 × 3)

Formation of Hydrogen Peroxide by Electric Discharge.—A. Besson.—To explain the presence of hydrogen peroxide in rain-water during thunderstorms, the author has investigated its formation by the electric discharge in conditions which resemble those naturally occurring, viz., in a cooled receptacle under decreasing pressures, With water-vapour alone and under pressures

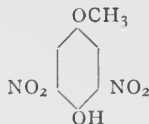
from that of the atmosphere to 30 mm., no colouration of chromic solution is observed. It oxygen is present H_2O_2 is formed when the pressure lies between the atmospheric pressure (770 mm.) and half this pressure. If air is substituted for oxygen the positive results are much less constant, owing probably to the simultaneous formation of oxygen compounds of nitrogen, which destroy the H_2O_2 . Thus it is proved that hydrogen peroxide is formed by the action of the electric discharge on rarefied damp air at a fairly low temperature, *i.e.*, under conditions which occur in the higher regions of the atmosphere.

Lactarinic Acid.—J. Bougault and C. Chavaux.—By applying Beckmann's classical method to the oxime of lactarinic acid, the authors have proved that the acid is the 6-ketostearic acid, and must be represented by the formula $\text{CH}_3-(\text{CH}_2)_{11}-\text{CO}(\text{CH}_2)_4-\text{CO}_2\text{H}$. The other two ketostearic acids which are known are the 9-acid, $\text{CH}_3-(\text{CH}_2)_8-\text{CO}-(\text{CH}_2)_7-\text{COOH}$, fusing at 83° , and the 10-acid, $\text{CH}_3-(\text{CH}_2)_7-\text{CO}-(\text{CH}_2)_8-\text{COOH}$, fusing at 76° . Lactarinic acid fuses at 87° .

Bulletin de la Société Chimique de France.
Vol. ix.-x., Nos. 20—21, 1911.

Hydrogenation of Crotonic Aldehyde in Presence of Nickel.—R. Douris.—The hydrogenation of crotonic aldehyde in presence of nickel (reduced from the oxide at 270°) at 175° gives nearly equal amounts of normal butyric aldehyde and butyl alcohol. At 125° 48 per cent of butyric aldehyde is formed and 20 per cent of butyl alcohol. In addition, at both temperatures a syrupy product is obtained; it has a slight smell, and boils at $115-119^\circ$ under 18 mm.; it probably contains an octyl alcohol, but it has not yet been obtained in sufficient quantity to isolate a pure substance from it.

Constitution of Monomethyl-ether of Weselsky and Benedikt's Dinitrohydroquinone.—F. Reverdin and A. de Luc.—The authors have already described a nitramine, fusing at 125° , of a dinitromonomethyl-*p*-anisidine; with caustic soda it yields the monomethyl ether of dinitrohydroquinone, already described by Weselsky and Benedikt. The nitramine on reduction gives a base which is identical with the *m*-diamine, and hence there is no doubt that the ether has the formula—

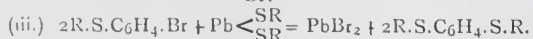
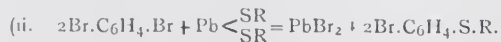


Monomethyl and Dimethyl-3,4-dioxybenzylamine.—M. Tiffeneau.—Monomethyldimethoxy-2,4-benzylamine can be prepared by heating together in a sealed tube the hydrochloric ether of veratric alcohol and an alcoholic solution of methylamine. When it is demethylated with concentrated hydriodic acid the product is monomethyl-3,4-dioxybenzylamine. The corresponding dimethyl base can be obtained by similar reactions, substituting a benzene solution of dimethylamine for the methylamine.

Formation of Aromatic Disulphides of Types R.S.R'.S.R and R.S.R'.S.R''.—E. Bourgeois and A. Fouassin.—When *p*-dibromobenzene acts on a mercaptide of lead, $\text{Pb}(\text{SR})_2$, the two atoms of bromine may either be replaced by the radicles S.R :—



or else the reaction may occur in two stages—

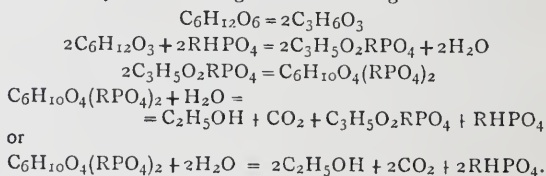


It is found that reactions (ii.) and (iii.) occur simultaneously at practically the same temperature. If excess of dibromobenzene is used some monobrom-sulphide is formed, according to equation (ii.), and is not converted into the disulphide.

Action of Bromonitro-benzenes on Thiophenates.—E. Bourgeois and P. Huber.—The sodium salt of phenyl mercaptan dissolved in absolute alcohol reacts with 1,4-bromonitro-benzene to give mononitrophenyl sulphide. The 1,2-bromonitrobenzene acts in the same way, but much more energetically. The 1,3-isomer behaves quite differently, since sodium bromide, which is formed in the first two reactions, is not produced in appreciable quantities. A black mass is obtained; it contains some unaltered *m*-bromonitro-benzene, a little phenyl disulphide, and a red crystalline substance which the authors have not obtained in sufficient quantity to identify. Apparently the presence of bromine is no obstacle to the entrance of an NO_2 group into the ortho or para positions, but when this group is introduced into the bromide molecule it tends to drive out the bromine. In the meta system NO_2 allows the bromine to occupy the position 3, but the bromine does not exhibit the same toleration towards the nitro group.

Catalytic Preparation of Aromatic Ketones.—J. B. Senderens.—In presence of thoria the *o*-, *m*-, and *p*-toluic acids (1 mol.) readily react with acetic acid (3 mol.) to give mixed aromatic ketones. The author has thus prepared the cresyl, methyl, ethyl, propyl, isopropyl, and isobutyl ketones. With each of these ketones the boiling-point rises as we pass from the ortho to meta and meta to para compound, and the density decreases. If one series is studied, either ortho, meta, or para, it is found that the boiling-point rises regularly with the molecular weight of the ketone, while the density decreases. For two isomeric ketones belonging to the same series the boiling-point falls as the molecule becomes more complex. Phenylpropionic acid also gives mixed ketones under the catalytic action of thoria.

Mechanism of Alcoholic Fermentation.—A. Lebedeff.—The author's experiments show that alcoholic fermentation takes place according to the following scheme :—



MEETINGS FOR THE WEEK.

MONDAY, 18th.—Royal Society of Arts, 8. (Cantor Lecture). "The Carbonisation of Coal," by Prof. Vivian B. Lewes.

WEDNESDAY, 20th.—Microscopical, 8. "Photomicrography of the Electrical Reactions of the Heart," by F. Shillington Scales. "British Tubificæ," by Rev. H. Friend.

THURSDAY, 21st.—Chemical, 8.30. "Investigations on the Dependence of Rotatory Power on Chemical Constitution—Part II., The Rotations of some Secondary Alcohols containing the Isopropyl Group," by R. H. Pickard and J. Kenyon. "The Alcohols of the Hydroaromatic and Terpene Series—Part II., The Menthols corresponding to Optically Inactive Menthone," by R. H. Pickard and W. O. Littlebury. "Absorption Spectra of Quinine, Cupreine, 6-Methoxy-quinoline, and 6-Hydroxy-quinoline," by J. J. Dobbie and J. J. Fox.

Congress of Pure and Applied Chemistry and Physics.—The President and Organising Committee of the second Congress of Pure and Applied Chemistry and Physics in honour of the late D. I. Mendéléeff, desire it to be known that the Congress will be held at the University of St. Petersburg from January 3rd to 10th next.

THE CHEMICAL NEWS.

Vol. CIV., No. 2717.

NOTES ON THERMOSTATS.*

By Prof. HUGH MARSHALL, D.Sc., F.R.S.

1. Electric Heating.

The great convenience, cleanliness, and safety of electric methods of heating have naturally led to their adoption by many experimenters for use in connection with thermostats, and there are already in the literature several descriptions of arrangements devised for this purpose. These fall into two main classes—one in which the heating is applied externally to the thermostat, as with gas heating, and the other in which the heating mechanism is immersed in the liquid of the thermostat. With the former a metal or metal-bottomed vessel has to be used, but when suitable internal heating is adopted any convenient vessel may be easily converted into a thermostat. With external heating, it is usual to employ an ordinary carbon-filament glow-lamp, or a battery of several; but with internal heating bare metallic wires or similar devices seem to have met with most favour.

I took up the question of electric heating some years ago, and came to the conclusion that bare wires, &c., were not suitable for thermostat work, but that some modified form of glow-lamp would be much superior; a number of special lamps were therefore ordered for the purpose, and were found to serve excellently; they are illustrated in Fig. 1. The bulb is at the end of a long

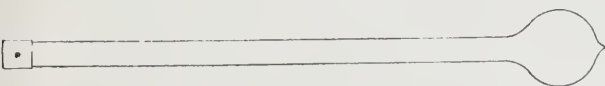


FIG. 1.

glass tube, the length over all being about 30 to 40 cm.; the other end of the tube is fitted with metal contact pieces, collar, and studs as on an ordinary lamp, so that connection with flexible leads can be secured by means of the usual lamp socket. Two copper wires, carried by glass supports, pass down the tube and make connection between the contacts and the filament. Since the whole is hermetically sealed, the lamp may be immersed in water almost up to the collar, without risk of short-circuiting or electrolytic corrosion. Seeing that no lighting effect but heating is wanted, there is no objection to such lamps being considerably under-run; there is, on the contrary, the great advantage of a greatly increased life. Lamps should therefore be ordered for a decidedly higher voltage than that of the circuit with which they are to be used; with a 200-volt circuit I specify 250-volt lamps, and a nominal candle-power of about 50. A single lamp of this kind is ample for an ordinary table thermostat.

In use, the lamp is simply gripped in an ordinary retort-stand clamp, and held vertically in the wooden, glass, or metal vessel used as thermostat; it is joined up with whatever appliance is used for switching the current on and off. To overcome the buoyancy, a ring of lead may be placed round the tube, resting on the bulb. A very convenient vessel for use as a bench thermostat in connection with an apparatus of this kind is an ordinary glass secondary-battery cell, of sufficient size. This particular vessel was first suggested by a former colleague, Dr. W. W. Taylor; up till then I had only used a small wooden tub.

As regards the regulators, &c., to be used, little need be said; many modifications are available. Hitherto I have

used one of Köhler's toluene regulators, provided with platinum-mercury contact having screw adjustment. This is, of course, not used directly to open or close the heating circuit, but actuates a relay. The relay is a simple post-office pattern, adapted with contacts of platinum wire and foil to close the heating circuit; the driving current for the relay is supplied by a single small accumulator cell, and, to ensure that this will never run down, it is joined up in the heating circuit. The connections are indicated in the diagram, Fig. 2, where C is the accumulator, R the relay, and L the heating lamp.

With the arrangement shown in the diagram, the relay comes into action when the temperature rises, and therefore is arranged to cut off the heating current. The accumulator is discharging during the whole time the heating current is cut off; when, however, the heating apparatus is in action the whole of the heating current passes through the accumulator, recharging it.

With a modified form of regulator the relay can be arranged to come into action when the temperature falls. In this case, as soon as contact has been made, the relay is kept in action by a fraction of the heating current; the greater portion of the current passes through the accumulator, since this has a much lower resistance than the relay. Except at the first moment of making contact, therefore, the accumulator either is out of action altogether, or is being charged by the heating current.

With an internal heating arrangement such as this, uniform temperature throughout can only be obtained

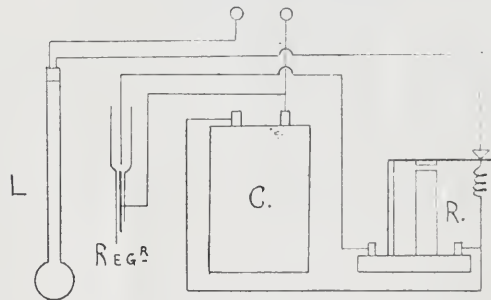


FIG. 2.

when some form of stirrer is used, but that need not be discussed here.

For long-continued work, especially if the thermostat is to be run night as well as day, it would be advisable to run two heating lamps in parallel, in case of the filament breaking; with greatly under-run lamps, however, there would not be much risk. Such a precaution might also be advisable in very cold weather, should the room temperature be liable to fall much during the night.

2. Ice Thermostats.

Many observers who have carried out series of experiments conducted nominally at the freezing-point of water seem to have experienced great difficulty in keeping the temperature down to 0°, the temperature actually maintained being about 0.3°. With suitable simple arrangements, however, there should be no difficulty whatsoever in keeping within less than 0.1° of zero. The great point to be observed is to keep a good supply of ice at the bottom of the thermostat; the following apparatus secures this, and has proved quite satisfactory in use. The description given is that of an actual apparatus, but, of course, there is room for a good deal of modification.

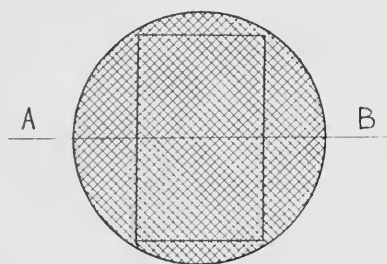
The thermostat consists of a cylindrical metal vessel (one of poorly-conducting material would, of course, be preferable), and was prepared by removing the conical top from a Kahlbaum 50-kilo. alcohol drum; it is about 50 cm. deep and 40 cm. in diameter, of fairly stout metal, and conveniently provided with handles. After being thickly

* A Paper read before the Faraday Society, December 6, 1911.

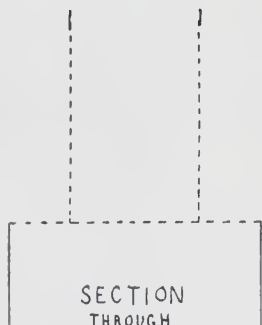
coated with black varnish inside and out, it was wrapped round with several layers of thick felt secured with wire. The thermal insulation of the bottom is important, and this is secured by standing the vessel in a wooden tray filled with sawdust to a depth of several inches.

A framework of stout perforated sheet zinc (also varnished) fits inside the vessel, having the form indicated in the sketches (Figs. 3 and 4). The lower part (which need not be perforated) is cylindrical, and fits *easily* inside the vessel; it is about 15 to 20 cm. high. Attached to it (above) is a circular sheet of perforated metal, which forms a kind of false bottom to the vessel; to this in turn is attached the rectangular upper part, about 30 to 35 cm. high and 30 by 20 cm. across. When the complete framework is inserted into the vessel, the tops of the two are on the same level.

To use the thermostat, it is placed in position on the tray (the framework being removed), and crushed ice is introduced to a depth almost equal to that of the lower



PLAN
FIG. 3.



SECTION
THROUGH
A—B

FIG. 4.

part of the framework; ice-cold water is then run in to a moderate depth, so as to float the ice, after which the framework is placed in position, imprisoning the ice; lumps of ice are next packed outside the rectangular part of the framework, right up to the top, after which the vessel is almost filled with ice-cold water; finally, a fine mush of pounded ice is placed inside the rectangular space, so as to float to a depth of 2 to 3 cm.

The inside of the rectangular space forms the working compartment; it can be fitted with suitable stirring apparatus if wanted, rotating or agitating appliances, tube-holders, &c. With the apparatus actually described it has been found that in an ordinary room a single complete charging will last over a period of two days, though it may be necessary to draw off some of the water and put more ice into the upper part within that period; once the ice in the bottom compartment is all melted it becomes impossible to keep the temperature down properly, no matter how much ice there may be above, and it is necessary to

recharge completely. With a larger (especially deeper) apparatus, giving increased storage capacity in the lower compartment, a longer serviceable period could doubtless be obtained if desired.

3. Thermostats for Temperatures between 0° and 20°.

Various devices have been tried for maintaining constant temperatures at some specified point intermediate between zero and one slightly above the ordinary temperature of the air, but they are generally cumbersome and rather unsatisfactory. As a consequence the determination of various constants at such intermediate temperatures (at the maximum density point of water, for example) is often omitted in cases where it would otherwise be carried out and be highly desirable.

The method of internally heating thermostats provides a simple means of overcoming the above mentioned difficulty; actually I have thus used it only for the temperature of 12.5° (*i.e.*, at a point midway between 0° and 25°, in order to have regular intervals in series of solubility determinations), but there seems to be no reason why it should not work quite well as far down as the maximum density point. The apparatus actually used consisted of the vessel already described as an ice thermostat, with the framework removed; inside it was placed a large secondary-battery cell, resting on bricks, so that its top was level with the top of the outside vessel. The glass cell was fitted up as an internally-heated thermostat and was filled with water almost at the desired temperature; the outer vessel was filled with water about 5° lower in temperature, and from time to time pieces of ice were introduced, so as to maintain it roughly at about that difference. The temperature of the inner thermostat can be easily and quickly adjusted, and thereafter it is only necessary to see that the whole of the ice in the outer vessel does not disappear; this only necessitates inspection at intervals of some hours, provided the ice is added in compact blocks and in amount appropriate to the difference between the working temperature and the temperature of the air. The consumption of ice is surprisingly small, provided the outer vessel is well insulated; the thick glass walls of the inner cell do not allow a rapid transference of heat to the water outside.

If such an apparatus were wanted for use at temperatures at or near the maximum density point it would probably be desirable to fit the glass cell inside the rectangular chamber of the framework already described, and by means of this to keep a supply of ice at the bottom of the outer vessel.

A MODIFIED PROCEDURE FOR THE DETECTION OF SILICATES, FLUORIDES, AND FLUOSILICATES.

By PHILIP E. BROWNING.

THE method for the detection of silica depending upon the formation of the insoluble skeleton of silica in the metaphosphate bead is not always satisfactory in the hands of the average student, and the method which depends upon the observation of the jelly of silicic acid on evaporation with hydrochloric or nitric acid is of course available only when the silicate is decomposed by those acids.

The formation of silicon fluoride by the action of hydrofluoric acid or a fluoride, and sulphuric acid upon a silicate is often applied to the detection of silica, since the silicon fluoride when acted upon by water gives a white precipitate of silicic acid. The usual procedure in making this test is to allow the gas to come in contact with a moistened glass rod, but the condensation of steam or sulphuric acid on the rod often makes the results uncertain.

The work to be described was undertaken to devise, if possible, a method by means of which the reaction could

be made more delicate and trustworthy. It was found that when moistened black paper was brought in contact with the fumes of silicon fluoride the deposit of silicic acid was very easily detected. Accordingly the following method was tried:—

A small lead cup about 1 cm. in diameter and depth was made by running the melted metal into a mould, and a flat piece of lead with a small hole in the centre was used as a cover. Into this cup a small amount of finely powdered calcium fluoride, generally about 0.1 grm., was placed together with the silicate, and the mixture covered with a few drops of concentrated sulphuric acid, added by means of a medicine dropper or fountain-pen filler. Upon the upper side of the cover a piece of moistened black filter-paper was placed, and upon this a small moistened pad of ordinary filter-paper was laid to keep the black paper moist during a heating of about ten minutes upon a steam-bath. At the conclusion of the heating a white deposit was found on the underside of the black paper over the opening in the cover, if silica was present in appreciable amount.

TABLE A.—Silicon Tests.

Name and amount of silicate used. Grm.	Approximate percentage of SiO ₂ .	CaF ₂ present. Grm.	Result.
1. 0.1000 SiO ₂	100	None	Nothing.
2. 0.1000 "	100	0.1000	Very good.
3. 0.0100 "	100	0.1000	Very good.
4. 0.0050 "	100	0.1000	Very good.
5. 0.0010 "	100	0.1000	Trace.
6. 0.0100 Kaolinite ..	46	0.1000	Very good.
7. 0.0050 "	46	0.1000	Very good.
8. 0.0010 "	46	0.1000	Trace.
9. 0.0100 Gadolinite..	24	0.1000	Very good.
10. 0.0050 "	24	0.1000	Trace.
11. 0.0100 Lepidolite..	50	0.2000	Good.

TABLE B.—Fluorine Tests.

Name and amount of fluoride used. Grm.	Approximate percentage of F.	SiO ₂ present. Grm.	Result.
1. 0.1000 CaF ₂	49	None	Nothing.
2. 0.0100 "	49	0.0500	Very good.
3. 0.0050 "	49	0.0500	Apparent.
4. 0.0010 "	49	0.0500	Trace.
5. 0.0100 Na ₃ AlF ₆ ..	54	0.0500	Very good.
6. 0.0050 "	54	0.0500	Distinct.

TABLE C.—Fluosilicate Tests.

Na ₂ SiF ₆ present. Grm.	Result.
1. 0.0050	Very good.
2. 0.0010	Very good.

pulverised, and the delicacy of the test seems to be also somewhat furthered by warming the sulphuric acid before adding it to the mixture of the fluoride and silicate. When fluosilicates are to be examined these precautions are not necessary, as the reaction with the sulphuric acid takes place quite readily in the cold.—*American Journal of Science*, xxxii., October, 1911.

THE CHEMICAL AND MECHANICAL RELATIONS OF IRON, CHROMIUM, AND CARBON.*

By J. O. ARNOLD, D.Met., and A. A. READ, M.Met.

THE paper gives details of experiments to determine—(1st) the composition of the carbides separated from a series of annealed steels containing various percentages of chromium, the percentage of carbon remaining practically

TABLE I.—Analyses of Specimens of Steel.

No. of steel.	Carbon. Per cent.	Chromium. Per cent.	Silicon. Per cent.	Phosphorus. Per cent.	Manganese. Per cent.	Sulphur. Per cent.	Aluminium. Per cent.
1147	0.64	0.65	0.04	0.02 or under	Under 0.10	0.02 or under	Under 0.01
1090	0.84	0.99	0.06				
1093	0.835	4.97	0.08				
1091	0.85	10.15	0.11				
1092	0.88	15.02	0.03				
1148	0.85	19.46	0.11				
1149	0.85	23.70	0.20				

TABLE III.

Bar No.	Yield point (tons per square inch).	Maximum stress (tons per square inch).	Elongation (per cent).	Reduction of area (per cent).	Carbon (per cent).	Chromium (per cent).
1147	20.52	43.2	24.5	40.56	0.64	0.65
1090	18.88	43.36	22.5	39.2	0.84	0.99
1093	16.12	37.80	31.5	63.9	0.84	4.97
1091	16.52	37.20	29.0	56.5	0.85	10.15
1092	20.80	43.92	20.0	36.00	0.88	15.02
1148	48.72	56.85	16.0	26.45	0.85	19.46
1149	34.80	49.52	12.0	21.5	0.85	23.70

Talbot has shown that very small amounts of fluorides may be detected by the etching test (*Journ. Am. Chem. Soc.*, xxviii., 1437). The converse of the method just described for the detection of silicates was applied to the detection of fluorides, and while extreme delicacy cannot be claimed, the results are fairly satisfactory when a mgrm. of fluorine is present.

The detection of fluosilicates by this method is, of course, even simpler than that of either the fluorides or the silicates. The results are given in Tables A, B, and C. From these results it is apparent that 1 mgrm. of silicon or fluorine may be detected by the method described.

When very small amounts of material are to be tested it is especially desirable to have the material very finely

the same in each; (2nd) the mechanical properties of the alloys under static and alternating stress tests; (3rd) the microscopical features of the alloys.

The alloys were cast into 2 in. square ingots, hammered and rolled into 1 in. round bars, and annealed; these were turned to 0.564 in. diameter for the static test-pieces, and to 0.375 in. diameter for the alternating test-pieces, and to the same dimensions for the carbide bars from which the micro-sections were machined.

The analysis of the specimens are given in Table I.

The carbides from Nos. 1147 and 1149 were bright and silvery. From Nos. 1093, 1091, 1092, and 1149 the

* Abstract of Paper read before the Iron and Steel Institute.

(a) Not the total weight of dry residue obtained; a small quantity was unavoidably lost.
(b) Owing to the rough state of the bars, after solution in the acid, it was quite impossible to remove all the carbide. Further, during the cleaning of the bars, thin bright strips of metal came away with the carbide. These strips of metal dissolved readily on treating the carbide residue with aqua regia in the cold. A sufficient quantity of carbide, however, was obtained from the two bars for the analysis given, and the slightly lower percentage of carbon registered is probably due to the aqua regia treatment.

No. of steel.	Carbon, Per cent.	Chro-mium, Per cent.	Ampere.	Volts at terminals.	Time in acid, Hours.	Grms. dissolved.	Weight of dry residue.	Percentage of total carbon obtained in the carbide residue.	Analysis of carbide.			Corresponding to the formula.	Theory.		
									Carbon, Per cent.	Iron, Per cent.	Chromium, Per cent.		Carbon, Per cent.	Iron, Per cent.	Chromium, Per cent.
1147	0.64	0.65	0.55	0.9 to 1.6	12	10.00 10.03 10.03	0.8742 0.9037 0.8912	94.28 99.37 98.84	6.95 7.08 7.12	88.93 88.35 88.47	4.12 4.56 4.41	20Fe ₃ C, Cr ₃ C ₂	6.98	88.88	4.13
1090	0.84	0.99	0.55	0.9 to 1.3	12	8.74 8.74 8.74	0.9016 0.8725 0.7113	85.72 82.17 85.54	7.20 7.27 9.04	85.80 85.51 45.20	6.99 7.22 45.67	12Fe ₃ C, Cr ₃ C ₂	7.18	86.15	6.66
1093	0.835	4.97	9.55	0.9 to 1.2	12	8.71 8.71 7.63	0.6667 0.6667 0.6918	80.73 80.73 87.05	8.66 8.66 8.16	45.52 45.52 28.38	45.81 45.81 63.51	4Fe ₃ C, 3Cr ₃ C ₂ , Cr ₄ C	8.92	45.40	45.67
1091	0.85	10.15	0.55	0.9 to 1.2	12	7.63 7.63 9.83	0.6918 0.6579 1.3989	87.05 81.77 97.41	8.16 8.23 6.05	28.38 62.83 34.60	62.83 62.83 59.34	Fe ₃ C, Cr ₃ C ₂ , Cr ₄ C	8.28	28.96	62.76
1092	0.88	15.02	0.55	0.9 to 1.4	12	9.79 9.80 9.97	1.4458 1.3746 (a) 1.6198	99.60 — 99.19	5.96 5.58 5.21	34.54 33.10 32.60	50.49 60.93 62.13	2Fe ₃ C, 3Cr ₄ C	5.85	32.94	61.18
1148	0.85	19.46	0.55	0.9 to 1.4	12	9.97 — (b)	1.6198 — (b)	99.19 — (b)	5.21 5.05	32.60 32.12	62.13 62.83				
1149	0.85	23.70	0.55	0.9 to 1.4	12	— (b)	— (b)	— (b)	5.05	32.12	62.83				

TABLE II.

carbides were slate coloured, and from 1148 the carbide was obtained as fine slate coloured needles.

The results of the analyses are given in Table II.

The results given in the table show that chromium replaces iron in the carbide, even when the steel contains only such a small quantity as 0.65 per cent of chromium.

The microscopical characteristics of the alloys are shown by a series of four photo-micrographs, alloys containing from 0.5 to 5 per cent of chromium show pearlitic structure embodying all the phases of pearlite; the occurrence of all these phases in one minute area of steel, which has been very slowly cooled from a full red heat, indicates the unscientific nature of a classification which attempts to discriminate between the various phases of pearlite by classing them as separate constituents.

Alloys with from 6 per cent of chromium and upwards consist of chromiferous ferrite containing particles of the double or triple carbide.

The tensile tests of the alloys are given in Table III., and the alternating stresses by Arnold's kinetic stress-strain test are given in Table IV.

TABLE IV.

Bar No.	Carbon (per cent).	Chromium (per cent).	Alternations endured.		
			1st test.	2nd test.	Mean.
1147	0.64	0.65	286	334	310
1090	0.84	0.99	342	376	359
1093	0.84	4.97	364	350	357
1091	0.85	10.15	298	312	305
1092	0.88	15.02	142	140	141
1148	0.85	19.56	76	64	70
1149	0.85	23.70	74	134	104

There is no correlation between the static and kinetic test results.

THE VOLUMETRIC ESTIMATION OF SULPHUR IN IRON AND STEEL.*

By T. GIFFORD ELLIOT (Sheffield).

THE methods used in the analysis of iron and steel twenty years ago were largely gravimetric, whereas the majority of those in use at the present time—at least in a works laboratory—are volumetric, although in the estimation of sulphur in iron and steel no volumetric process has yet been discovered which is universally applicable, and the gravimetric process known as the "aqua regia" is still in constant use.

Whether the "aqua regia" or Bamber's method be used, the gravimetric estimation of sulphur is very tedious, and liable to error even in skilful hands. This is proved by the difficulty of obtaining results in agreement from different laboratories on the same sample, although variations in the method of working are probably responsible for some of the discrepancies.

The volumetric estimation of sulphur has received considerable attention during the last few years, and many papers have been written on the subject. Most of the work has been devoted to eliminating the loss of sulphur in the evolution method, generally thought to be due to the formation of organic sulphur compounds instead of sulphuretted hydrogen, on attacking the metal with acid.

Various suggestions have been made with a view to effecting this most necessary result. The chief are as follows:—1. The speed of solution should be as quick as possible. 2. The gases from the evolution flask should be passed through a hot tube to decompose any organic sulphur compounds, and then into an absorption flask. 3. The weighed portion of the sample should be annealed in a non-oxidising atmosphere before treatment with acid. 4. The acid used to dissolve the metal should be concentrated hydrochloric acid of 1.19 specific gravity.

* A Paper read before the Iron and Steel Institute.

Schulte (CHEMICAL NEWS, lxxv., 47) and also Phillips (*Journ. Soc. Chem. Ind.*, 1896, p. 218) in 1895 suggested passing the gases through a red-hot tube.

In 1902 Walters and Miller first suggested the annealing of the weighed portion for analysis before treatment in the evolution flask (*Journ. Iron and Steel Inst.*, 1902, No. 1, p. 851). They placed the sample in a porcelain boat, and heated to bright redness in a tube in a current of hydrogen for fifteen minutes, but if the sample contained an "appreciable amount of titanium," for half-an-hour.

In the same year Dougherty made the annealing more practicable, by suggesting the use of a covered porcelain crucible for the purpose, with a piece of filter-paper placed on the drillings to provide the non-oxidising atmosphere (*Iron Age*, May 8, 1902, p. 14).

C. A. Seyler (*Analyst*, April, 1903) described his experiences with Dougherty's method in a paper read before the Society of Public Analysts in December, 1902. He obtained the best results by annealing at 750° C., although he stated that more experiments were required to obtain the best temperature. So far as I am aware, this is the only published instance where the temperature of annealing was measured.

S. S. Knight (CHEMICAL NEWS, xc., 326) modified Dougherty's method in 1904, by mixing the sample with pure iron dust reduced by hydrogen. The mixture was placed in a porcelain crucible, covered with a little more iron dust and an ashless filter-paper. The lid was put on, and the whole heated for ten minutes "at the highest heat obtainable by a blast-lamp."

In 1906 J. MacFarlane and A. W. Gregory suggested the use of cream of tartar to mix with the drillings for annealing (CHEMICAL NEWS, xciii., 201). They mixed 5 grms. of the powdered sample with half a gm. of cream of tartar, wrapped the drillings in filter-paper, placed in a small porcelain crucible, covered, and annealed at a bright red heat in a muffle for fifteen minutes.

An interesting report was presented in 1908 by H. Kinder (*Stahl und Eisen*, 1908, No. 8, p. 249), of the work of a Chemical Commission appointed by the German Society of Ironworkers, to inquire into the estimation of sulphur in iron and steel. The figures obtained show that the highest results were got by the use of strong hydrochloric acid, 1.19 specific gravity, and quick evolution, and that under these conditions the use of a red-hot tube is unnecessary.

In a laboratory where the ordinary routine consists in the analysis of samples varying from the best hæmatite iron to high phosphorus foundry iron, and from the purest transformer iron through the many varieties of steel used for steel castings to complex alloy steels, the applicability of a method for general use is severely tested.

I have found that many samples of iron and steel do not evolve their full sulphur contents after merely annealing in a non-oxidising atmosphere when treated with concentrated hydrochloric acid. MacFarlane and Gregory's method of annealing with cream of tartar, however, gave me excellent results with some brands of iron with which I had previously not succeeded; but with other brands, and particularly with nickel-chromium steels and other self-hardening material, for which I was very anxious to find a quick method of determining the sulphur, the full amount was not obtained. I am not overlooking the fact that the method was only designed for irons.

My experience agrees with the finding of the German Commission as to the importance of using concentrated acid and rapid evolution. Moreover, in many experiments, I passed the gases from the absorption flask through a red-hot tube and into a second flask, but the amount of sulphide obtained in the second solution was negligible.

In order to find a more active reagent than cream of tartar, I tried various substances, and finally chose potassium ferrocyanide. The effect of heat upon this substance is to decompose it into carbide of iron, potassium cyanide, and nitrogen. The result is, that the

drillings are more or less carbonised, and a strongly reducing atmosphere obtained.

Experiments made to determine the length of time required for annealing indicated that, with less than twenty minutes, low results are obtained. On the other hand, no advantage is usually to be gained by exceeding this period, whilst, in the case of steel drillings, oxidation is then liable to occur.

Annealing experiments with different amounts of ferrocyanide indicated that 0.25 gm. mixed with 5 grms. of the sample was the most suitable amount. If more is used, cyanogen compounds may be driven into the absorption flask, especially if the condensing tube gets hot. The result is, that when the titration is made by adding iodine to the contents of the absorption flask without filtering, acidified only with acetic acid, an excess of iodine may be added beyond that required to dissolve the sulphide, without any colour being imparted to the solution. (A drop of starch solution added here gives the characteristic blue colour). On adding dilute hydrochloric acid, the brown colour due to the excess of iodine appears, and the titration is proceeded with as usual, the result being unaffected, notwithstanding.

Experience has shown that in order to obtain correct results it is absolutely necessary to control the temperature of annealing. As will be seen from the table of results, the correct temperature lies between 750° C. and 850° C.

If there are no means of measuring the temperature available, it is necessary to work a standard of known sulphur content with each batch of samples annealed.

An indication as to whether the sulphur is being evolved correctly is furnished by the colour of the precipitated cadmium sulphide. This should be distinctly yellow. A pale precipitate is usually associated with a low result, and suggests that the annealing has not been conducted properly.

In order to promote uniformity in the rate of solution, which is important, it is advisable that the drillings of the sample should be of the same degree of fineness as the standard, and of similar composition. Reference is made below to the use of a standard.

The method I have adopted is as follows:—Five grms. of the sample are mixed, as far as is practicable, with 0.25 gm. of pure finely powdered anhydrous potassium ferrocyanide, and wrapped in one 11 cm. filter-paper if the sample is a graphitic iron, or two papers if it is a steel or white iron, placed in a small porcelain crucible (Royal Berlin O.A.), covered with the lid, and annealed at 750° C. to 850° C. for twenty minutes in a closed muffle. After the annealing and subsequent slow cooling outside the muffle, the drillings should still be covered practically completely by the charred filter-paper, if the temperature has not been above 850° C. or they have not been in the muffle too long. I make a point of observing the appearance of the annealed drillings very closely, because low results are obtained if the paper is completely burnt away from the top of them. After cooling, the crucible is emptied into a glass mortar, and the slightly caked drillings loosened with a pestle. They are then brushed on to a small piece of stiff paper, which is rolled into cylindrical shape so that it will fit right into the neck of the evolution flask, and allow of the drillings being transferred to the flask without touching its neck or sides. The evolution flask is connected with a condensing tube 6 inches by 1 inch, containing about 2 inches of water, and standing in a conical beaker filled with cold water. A tube from this dips into a flask containing 60 cc. of the cadmium chloride solution, which again is connected with another flask containing more cadmium solution. Fifty cc. of concentrated hydrochloric acid are now added, and heat is immediately applied to the flask until the frothing of the contents indicates that the solution is well in progress. The flame of the burner used to heat the flask is now lowered. As soon as the speed of the bubbles of gas passing through the cadmium solution begins to slacken, the flame of the burner is raised so that the liquid in the

TABLE OF RESULTS.

Description of sample.	Gravimetric method. Sulphur per cent.	Evolution method. Sulphur per cent.							Special treatment.
		Unannealed.	Annealed (temperatures).						
			700° C.	750° C.	800° C.	850° C.	900° C.	950° C.	
Steel, No. 8620 ..	0.061	{ 0.025 0.026	0.046 0.045	0.058 0.058	0.061 0.060	0.059 0.059	0.053 0.054	0.046 (a) 0.051 (b)	—
Steel, R. 4290 ..	0.051	{ 0.030 0.031	0.045 0.048	0.049 0.050	0.051 0.051	0.050 0.047	0.048 0.046	—	0.050 (c)
Steel, No. 8672 ..	0.054	0.053	—	—	{ 0.053 0.054 }	—	0.048	—	{ 0.054 0.055 } (c)
Iron, No. 471 ..	0.085	{ 0.085 0.086	0.083 0.087	— 0.085	0.084 0.085	0.080 0.081	0.066 0.071	—	0.084 (c)
Iron, No. 726 ..	0.053	0.028	—	0.052	0.051	0.048	—	—	0.051

(a) Paper burnt off; drillings slightly oxidised.

(b) Drillings quite bright after annealing, instead of grey, as is the case when annealed at a lower temperature.

(c) The duplicate results were obtained by different workers, using different apparatus.

flask just boils. The boiling is continued so long as any appreciable amount of gas is given off from the solution. The apparatus is then disconnected, and iodine solution added in excess to the contents of the absorption flask—usually nothing is found in the safety flask; then 10 cc. or so of diluted hydrochloric acid (one part acid and two parts water) are added, and the liquid shaken to complete the solution of the sulphide. The excess of iodine is then titrated with sodium thiosulphate, starch solution being added when the iodine colour has nearly disappeared. (The air in the apparatus may be washed out by carbonic acid before the addition of the acid to commence with, and again at the end of solution of the drillings, if desired, though the slight advantage gained thereby is hardly worth the extra trouble for works practice).

If the filter-paper used to wrap the drillings, or the ferrocyanide itself, contain sulphates, the latter are reduced during the annealing, and their sulphur given off as sulphuretted hydrogen in the evolution flask, so that a blank determination becomes necessary. The blank can be conveniently determined upon a pure iron, by dissolving 5 grms. of the iron in concentrated hydrochloric acid, and absorbing the sulphuretted hydrogen as usual. By annealing another 5 grms. of the iron in the usual way, and determining the sulphur contents as in the direct estimation, any difference due to the above causes can be determined.

The iodine and thiosulphate solutions may be standardised by means of a steel or iron, the sulphur contents of which have been accurately determined by the "aqua regia" or Bamber's method. The value of the solutions in sulphur so obtained should agree closely with that got by calculation after standardising the thiosulphate against a standard solution of potassium permanganate. The latter is very easily performed, and is a very useful check on the working of the process. The solutions of iodine and thiosulphate used are of such strength that 1 cc. equals 0.005 per cent sulphur on 5 grms. of the sample.

The cadmium chloride solution is prepared by dissolving 20 grms. of cadmium chloride in water with the aid of a few drops of hydrochloric acid. Ammonia is added until the precipitate of cadmium hydrate formed completely dissolves. Acetic acid is then added until the solution becomes slightly acid, when a further 20 cc. are added in excess, and the solution made up to 2 litres.

I find the cadmium solution acidified with acetic acid, and containing ammonium acetate, the best absorbent to use. It does not absorb the hydrocarbons, phosphides, &c., simultaneously evolved with the sulphur compounds, to the extent that solutions of salts of zinc, lead, and copper do, or as do the alkaline solutions frequently used for this purpose. I have frequently tested the point by filtering off the cadmium sulphide before titration, and comparing the

results obtained by titrating the washed sulphide with those got by direct titration.

With reference to the table of results, the three steels each contain over 1 per cent of both nickel and chromium. No. 8620 is in the cast condition, R. 4290 in the tempered, and No. 8672 in the annealed state. The latter contained under 0.05 per cent of hardening carbon, and practically the whole of the sulphur was obtained as cadmium sulphide by direct evolution. This is most important, and I believe that therein lies the solution of the problem of how to obtain the whole of the sulphur in a sample of iron or steel evolved as sulphuretted hydrogen by hydrochloric acid.

Iron No. 471 was found to give off the whole of its sulphur as sulphuretted hydrogen by direct evolution (*i.e.*, without any preliminary treatment).

As it is my custom to have all iron samples annealed before treatment in the evolution flask, I experimented with this sample in order to test the effect of the annealing on the amount of sulphur obtained. The results are given in the table.

It is, of course, absolutely necessary that the sample should be completely decomposed by the acid. In the case of irons containing titanium, as Blair has shown (*Trans. Am. Inst. Min. Eng.*, xxxi., 748), this is not the case, and some of the sulphur may remain in the evolution flask in the insoluble residue. I have experimented with an iron containing 0.2 per cent of titanium. The sulphur content, obtained by a gravimetric method which included the fusion of the insoluble graphitic residue after treatment with aqua regia, was 0.080 per cent. The direct evolution gave 0.017 and 0.018 per cent. After annealing at 800° C. the amount obtained was 0.066 per cent.

The sample, after the special treatment described below, gave 0.076 per cent, which suggests that by a proper preliminary treatment the whole of the sulphur may be obtained even from pig-iron containing titanium by the evolution process.

The special treatment (referred to in the last column of results in the table) consisted in placing the crucible containing the sample in the muffle at 950° C., and leaving at that temperature for five minutes. The gas was then turned off, and the muffle allowed to cool down to just below 800° C. The gas was then re-lighted, and the temperature of the muffle kept at about 790° C. for fifteen minutes. The crucible was then brought out to the front of the muffle, and allowed to cool slowly.

I wish to express my thanks to Messrs. G. B. Willey, A.R.S.M., and E. J. Barnes (the latter of whom has been responsible for the control of the annealing), to whom I am indebted for the carrying out of a large amount of the experimental work involved in the preparation of this paper.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 7th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Lapworthura: a Typical Brittlestar of the Silurian Age; with Suggestions for a New Classification of the Ophiuroidea.*" By Miss I. B. SOLLAS and Prof. W. J. SOLLAS, F.R.S.

"*Physiological Influence of Ozone.*" By LEONARD HILL, F.R.S., and MARTIN FLACK.

Ozone, in concentrations of one part in a million and more, acts as an irritant to the respiratory tract, and diminishes the respiratory metabolism as shown by the lessened output of carbonic acid and the diminished fall in body weight, which occur both during the period of administration and for some time after. Concentrations of several parts per million cause acute inflammatory congestion of the lungs, and animals die as the result of this if kept long exposed to the ozone. Concentrations which can just be sensed by smell, i.e., far less than 1 part per million, have no injurious effect, and can be used safely in systems of ventilation. Injurious concentrations of ozone, by producing irritation of the air-passages, cough, and headache, compel anyone exposed to such to remove himself from the influence of ozone before any serious damage is done to the respiratory tract.

Very low concentrations of ozone mask disagreeable smells, give a fresh quality to air vitiated by such smells, and vary the depressing monotony of air which is artificially warmed. Ozone may possibly have some use in the treatment of disease of the respiratory tract if used in concentrations which produce a slight irritation and thus bring more blood and tissue lymph to the part.

"*Factors concerned in Agglutination.*" By H. R. DEAN, M.A., M.B., &c.

1. If, to a mixture of sheep corpuscles with antiserum so dilute that no agglutination is visible, be added a solution of globulin obtained from normal guinea-pig serum, the corpuscles are markedly agglutinated. By use of suitable controls it can be demonstrated that neither the globulin solution nor the dilution of antiserum employed are of themselves capable of agglutinating the corpuscles.

2. The substance present in the globulin solution which aids agglutination is relatively thermostable, and its presence can be demonstrated in whole heated guinea-pig serum.

3. Corpuscles, sensitised and washed to remove free antibody, can be agglutinated by the globulin solution. If, after agglutination has taken place, the corpuscles be removed with a centrifuge, the supernatant fluid can be shown to have lost its agglutinating property.

4. The agglutinating power of an extremely dilute antityphoid serum can be increased by addition of globulin solution. Adding this to a mixture of emulsion of *B. typhosus* with a dilution of antiserum too weak by itself to agglutinate bacilli, distinct agglutination can be obtained.

5. Formation of a specific precipitate by interaction of serum and homologous antiserum depends on presence in the mixture of a relatively large amount of antiserum. If, to a mixture of serum with antiserum so diluted that it is no longer able to produce a precipitate, is added the globulin solution, a definite turbidity is produced.

6. Probably agglutinating serum (antiserum) contains two factors, both of which are necessary to produce agglutination; one of these is the specific antibody, the other is a non-specific substance, possibly serum globulin. The interaction of antigen with antibody produces an aggregation of molecules of non-specific substance which may ultimately result in formation of definite turbidity.

This process of aggregation of the particles of non-specific substance is an essential part of the process of agglutination. It is possible to make a dilution of an antiserum which contains sufficient of specific anti-substance but not sufficient of non-specific substance. Deficiency in non-specific substance can be made up by addition of globulin solution obtained from normal serum.

"*Action of Dissolved Substances upon the Autofermentation of Yeast.*" By ARTHUR HARDEN, F.R.S., and S. G. PAINE.

All dissolved substances which plasmolyse the yeast-cell also cause a large increase in the rate of autofermentation. Substances such as urea, which even in concentrated solution do not produce plasmolysis, have no accelerating effect. Toluene produces a similar effect to concentrated salt solutions. The effect produced by salts is probably a direct result of the concentration of the cell contents due to plasmolysis, but in the case of toluene it is possible that some other factor (such as disorganisation of the cell, or hormone action) is concerned.

"*Further Experiments upon the Blood Volume of Mammals and its Relation to the Surface Area of the Body.*" By Prof. GEORGES DREYER and W. RAY.

"*Origin and Destiny of Cholesterol in the Animal Organisms.* Part VIII. *On the Cholesterol Content of the Liver of Rabbits under Various Diets and during Inanition.*" By G. W. ELLIS and J. A. GARDNER.

The authors have made analyses of the livers of a number of rabbits fed on the following diets:—Cabbage, bran which had been extracted with ether, extracted bran to which cholesterol had been added. In some cases the cholesterol, instead of being given with the food, was injected in olive oil solution into the peritoneal cavity. For animals fed on extracted bran alone the total liver cholesterol per kilogram of body weight is very constant, but when cholesterol is given with the food or injected into the peritoneal cavity a considerable increase takes place. A similar increase was observed in the liver cholesterol during inanition, when the animal lives on its own tissues. The percentage cholesterol content of the livers of newly born animals is of the same order as that of normally fed adults.

The results afford support to the working hypothesis, with regard to the origin and destiny of cholesterol in the organism, put forward some time ago by the authors, viz., that cholesterol is a constituent constantly present in all cells, and when these cells are broken down in the life process the cholesterol is not excreted as a waste product, but is utilised in the formation of new cells. A function of the liver is to break down dead cells, e.g., blood corpuscles, and eliminate their cholesterol in the bile. After the bile has been poured into the intestine in the processes of digestion, the cholesterol is re-absorbed, possibly in the form of esters, and carried in the blood stream to the various centres and tissues for reincorporation into the constitution of new cells.

CHEMICAL SOCIETY.

Ordinary Meeting, November 16th, 1911.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 288).

302. "*Some α'-Derivatives of Camphor.*" By JAMES ERNEST MARSH.

When bromine acts on camphor mercuribromide, $C_{10}H_{15}O, HgBr$, the main product besides mercury bromide is α'-bromocamphor. Hence in the monomeric derivatives of camphor the mercury occupies the α'-position. The author has shown (*Trans.*, 1910, xcvi., 240) that in the dimercuri-compounds the αα'-position is occupied by the mercury. When therefore the mono- are obtained from the di-derivatives the mercury in the α-position is

replaced by hydrogen, whilst that in the α' -position remains. The production of α' -bromocamphor in another way and its properties have been already described by the author (*Trans.*, 1890, lviii., 528). Whereas the crystals of ordinary α -bromocamphor show double refraction, Mr. T. V. Barker has found that α' -bromocamphor gives singly refracting crystals.

303. "The Velocity of Addition of Alkyl Bromides to Cyclic Tertiary Bases." By FRANK STEVENSON LONG.

The rates at which various alkyl bromides, especially *isoamyl*, *isobutyl*, and *isopropyl* bromides, combine with pyridine, α - and β -picolines, and quinoline in amyl alcoholic solution have been determined at 92.6°.

It was found that *isoamyl* bromide reacts, on the average, seven times, and *isopropyl* bromide three times, more rapidly than *isobutyl* bromide. These results, on comparison with those of other workers, seem to indicate that *isopropyl* compounds, owing to their secondary nature, are not strictly comparable with *isobutyl* and *isoamyl* compounds, since with some reagents they are more, and with others less, reactive than the other alkyl bromides. Except for this there is manifested considerable regularity explicable on steric hypotheses.

304. "The Essential Oil of *Origanum hirtum*, Link." (Preliminary Note). By SAMUEL SHROWDER PICKLES.

The *Origanum* oils are mostly obtained from countries bordering on the Mediterranean, and the two chief varieties known in commerce are (1) Trieste *origanum* oil, and (2) Smyrna *origanum* oil. It has long been assumed that the former is the product of *O. hirtum*, Link, and an oil was examined by Jahns in 1879 (*Arch. Pharm.*, 1879, ccxv., 1) which was obtained from a plant identified by Grisebach as *O. hirtum*, Lk. This oil consisted mostly of carvacrol, no thymol being found in it.

Early in the present year a consignment of herb described as "Origanum Plant" was received at the Imperial Institute from the Trieste Commercial Museum. Specimens of this material were identified at the Royal Gardens, Kew, as *O. hirtum*, Link. On chemical examination, however, the phenolic constituents of the oil obtained from this plant by distillation with steam were found to consist almost entirely of thymol, carvacrol being apparently absent.

The dry plant yielded 3.3 per cent of a pale yellow oil, which possessed a pronounced odour of thymol and a burning taste. It gave the following results on examination:— $D_{15}^{20} 0.9440$, n_D^{20} (in 100 mm. tube) $+0.24'$. The oil was soluble to a clear solution in 2.8 parts of 70 per cent alcohol. An estimation of the phenols present by absorption in dilute sodium hydroxide solution gave 64.4 per cent by volume, equivalent to 66–67 per cent by weight.

A determination of the thymol present by conversion of the latter into its iodine derivation gave 68.4 per cent of thymol (by weight). On seeding the original oil with a crystal of pure thymol, it rapidly deposited large quantities of this substance in beautiful crystals and in an approximately pure condition. The phenolic portion of the oil separated by means of sodium hydroxide solidified completely. Traces of another phenolic substance which gave a deep red coloration with ferric chloride were also observed.

This oil appears to be very similar to one recently examined by Schimmel and Co. (*Report*, October, 1911, p. 63).

305. "The Essential Oil of Dalmatian White Thyme." (Preliminary Note). By SAMUEL SHROWDER PICKLES.

A supply of this herb has recently been received at the Imperial Institute from the Commercial Museum of Trieste. Specimens of the plant were submitted to the Royal Gardens, Kew, for botanical examination, and it was there identified as *Satureia*, sp., possibly one of the many forms of *S. montana*, Linn., which is often difficult to distinguish from *S. cuneifolia*, Tenore.

The dry herb, when distilled in a current of steam,

yielded 1.64 per cent of an oil possessing the characteristic odour of carvacrol. It had a sharp burning taste, and a golden yellow colour. The oil had $D_{15}^{15} 0.9548$, $n_D^{15} 1.503'$, and contained 68.75 per cent of phenolic constituents, mostly carvacrol (nitroso-compound, m. p. 153–154°). The oil was soluble to a clear solution in 2.7 parts of 70 per cent alcohol. The non-phenolic constituents of the oil are under examination.

This oil appears to be very similar to one recently examined by Schimmel and Co. (*Report*, October, 1911, p. 109).

306. "The Molecular Configuration of 1-Methylcyclohexylidene-4-acetic Acid and of the Oxime of cyclohexanone-4-carboxylic Acid." By ARTHUR ERNEST EVEREST.

In their paper on "Optically Active Derivatives of 1-Methylcyclohexylidene-4-acetic Acid" (*Trans.*, 1911, cxix., 1510) Perkin and Pope summarily dismiss the points raised by the author (*CHEM. NEWS*, 1909, c., 295) regarding the correctness of their view (Perkin, Pope, and Wallach, *Trans.*, 1909, xcv., 1789) that the compound under discussion contains no asymmetric carbon atom.

In view of the fact that the matter is of some considerable importance—Perkin and Pope in their paper (*Ibid.*, p. 1511) say:—"The discovery of the new type of optically active substances referred to involves a considerable extension of the whole subject of stereochemistry"—the authors feel that a few further words on the subject will not be out of place.

From the outset the author wishes to point out that, as has already been mentioned in the Chemical Society's Annual Reports for 1909, his views are quite readily applicable to the case of the oxime of cyclohexanone-4-carboxylic acid (III.), described by Mills and Bain (*Trans.*, 1910, xcvi., 1866). and regarding which they say (*loc. cit.*):—"These substances may possess a certain interest in that they provide another example of compounds of which, like *d*- and *l*-inositol, and *d*- and *l*-1-methylcyclohexylidene-4-acetic acids (Perkin, Pope, and Wallach, *loc. cit.*), the molecular asymmetry is more fittingly defined with reference to the configuration of the molecule as a whole than expressed in terms of the presence of some 'asymmetric' atom."

The criticism contained in the author's previous paper (*loc. cit.*) was summed up in two alternative questions; Perkin and Pope have not satisfactorily answered either, but as justification for their claims they make three remarks, which, however, have no such effect.

Their first remark (*loc. cit.*) reads:—"An asymmetric atom is never the cause of optical activity; optical activity is apparently invariable, and asymmetry of a carbon atom is, in special cases, the result of enantiomorphism of molecular configuration. Optical activity and the presence in the molecule of an asymmetric atom cannot be considered as mutually related in the sense of cause and effect." This statement compared with one made in their former paper on this subject, and which reads thus:—"The optical activity is, in fact, not, as is still sometimes stated, due to the presence of an asymmetric carbon atom, but originates in the enantiomorphous molecular configuration," gives the whole of their position.

If, now, the contention of Perkin and Pope be proved correct, namely, that they, and Mills and Bain, have indeed produced compounds showing optical activity, yet containing no asymmetric atom within their respective molecules, then the author agrees that the above statements must be accepted; but, the author has shown—and in the present paper further supports his contentions—that both of the substances under discussion do contain an asymmetric carbon atom within their respective molecules. This being so, the author is of the opinion that the evidence bearing on this subject in literature is more likely to support his statement that it is a "generally accepted theory that the optical activity of a substance is due to the presence in it of an asymmetric atom," than to support the

above statements of Perkin and Pope. On the other hand, the author would point out that such evidence as has thus far been gathered cannot be said to prove either of these statements.

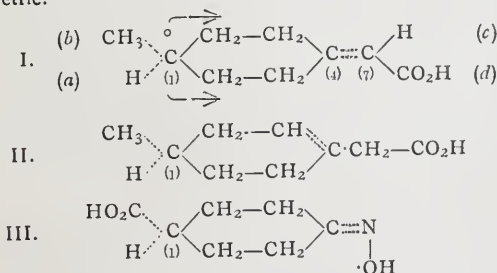
In connection with this, however, it is of interest to read a few lines which, if not written by Perkin, must at least have been assented to by him; thus on p. 544 of "Organic Chemistry," by Perkin and Kipping, we read:—"That the property of rotating the plane of polarised light is *due* to the presence in the molecule of an asymmetric carbon atom is now practically proved by the fact that all optically active compounds of known constitution contain a carbon atom united in this way. . . ."

Now Perkin's change of view was quite natural when describing what was then thought to be the first case of an optically active substance in the molecule of which there was no asymmetric atom, but, now that the substance has been shown to contain an asymmetric carbon atom within its molecule, does not the work only strengthen the proof spoken of in the passage from Perkin and Kipping referred to above?

In their second statement [*loc. cit.*, (b), p. 1511] the first portion makes it quite clear that Perkin and Pope admit the author's contention that the configuration of the remainder of the molecule is different when taken either way, relative to the carbon atom (1), for they deny having made the assumption that it was not so. In the second portion they give what is, presumably, their reason for considering—despite their statement in the first portion of this remark—that carbon atom (1) is not asymmetric. The author shows elsewhere in this paper that such an argument cannot stand.

Their statement (c), by reason of partial quotation, is not a true representation of the author's views. His view is, that carbon atom (1) of 1-methylcyclohexylidene-4-acetic acid has each of its four valencies differently occupied, and is hence asymmetric. This view is quite clear in his former paper, and had Perkin and Pope even considered the whole of their original quotation from that paper, instead of only a small portion, they could not have failed to see this point.

Now referring to the formula of 1-methylcyclohexylidene-4-acetic acid (I.)—as previously, continuous lines represent bonds in the plane of the paper; broken lines bonds in a plane perpendicular to the first, and passing through carbon atoms (1), (4), and (7)—in his previous paper the author clearly pointed out that, in his opinion, carbon atom (1), whilst having two of its valencies attached to the hydrogen atom (a) and the methyl group (b) respectively, has the remaining two valencies (those forming part of the ring) attached to different systems, and hence, being attached to four quite dissimilar groups, is asymmetric.



This, it will be seen, very much resembles the manner in which Perkin and Pope (with Wallach) pointed out that carbon atom (1) in inositol was an asymmetric carbon atom (*loc. cit.*).

Now that Perkin and Pope [remark (b)] admit that the configuration of the 1-methylcyclohexylidene-4-acetic acid molecule, taken respectively in the direction of $\curvearrowright$ and in the direction of $\curvearrowleft$ relative to carbon atom (1),

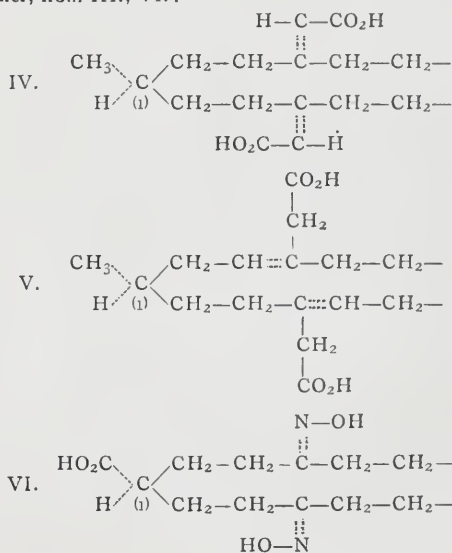
is not identical, it remains only to be shown that the difference is such that the carbon atom (1) is in the ordinary sense asymmetric.

Now to do so it is but necessary to compare the case of Marckwald and Meth's 1-methyl- Δ^3 -cyclohexene-4-acetic acid (II.), regarding which Perkin and Pope (*loc. cit.*) say:—"As the carbon atom numbered (1) in the latter constitutional formula is obviously attached to four constitutionally dissimilar groups, it is asymmetric in the ordinary sense."

Now, in making comparisons, the rings only need be considered, for, taking carbon atom (1) in formulae I. and II., it is seen that in each case the two valencies which are outside the ring have attached to them a methyl group and a hydrogen atom. In formula III. the methyl group is replaced by carboxyl.

Hence, if the difference shown between the two systems attached to carbon atom (1) and formed by the ring is in the case of 1-methylcyclohexylidene-4-acetic acid similar to that shown in the case of 1-methyl- Δ^3 -cyclohexene-4-acetic acid, then Perkin and Pope must surely admit that, on their own reasoning, the molecule of 1-methylcyclohexylidene-4-acetic acid contains an asymmetric carbon atom, the carbon atom (1).

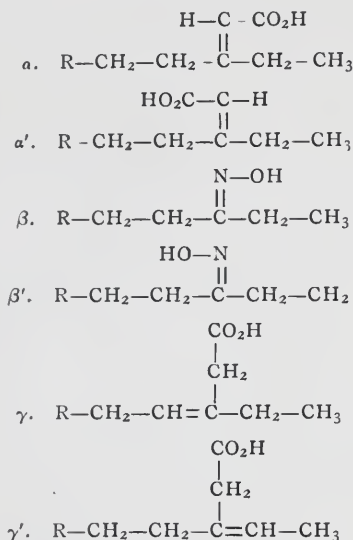
Now, treating the groupings as previously—and for that matter very much as done by Perkin, Pope, and Wallach for inositol—we get, on swinging open the ring of each molecule right and left, from I., IV.; from II., V.; and further, from III., VI.:—



Now it is quite clear that in none of these cases, as they stand, are the two chain systems formed from the ring enantiomorphously related. In no way while remaining attached to the carbon atom (1) can they appear in the relation of object and mirror image; whilst, if they be detached from the carbon atom, they are *identical*. This is true of each of the three cases shown in IV., V., and VI. respectively.

Hence it is seen that in reality, in each case, we are dealing with *one* system, but that that system is so constructed that the configuration relative to one end of the chain is different from that relative to the other end. The author therefore points out that, in his opinion, the differences thus shown in the systems attached to carbon atoms (1) in formulae IV. and VI. must be considered to make those carbon atoms [(1) and (1)] asymmetric, if it is allowed that the differences shown by the two similar systems in formula V. make carbon atom (1) of that formula asymmetric.

In support of this it may be pointed out that the compounds represented by α and α' and by β and β' would be expected to differ, α from α' and β from β' , just as surely as γ would be expected to differ from γ' . (R not = H).



Thus it is seen that the original conclusion of Perkin, Pope, and Wallach (*loc. cit.*) that in 1-methylcyclohexylidene-4-acetic acid they have realised "the first case of an optically active substance which possesses an enantiomorphous molecular configuration, although its constitutional formula contains no asymmetric atom, cannot be upheld, the methods used by them in removing Marckwald and Meth's acid and inositol from the field having been sufficient, when carefully applied, to trace the presence of an asymmetric carbon atom, both in the compound that they describe and also in that described by Mills and Bain. These compounds, therefore, are not centroasymmetric. Finally, it is necessary in this connection to consider a statement made by Perkin and Pope in their recent paper (*loc. cit.*) regarding the 4-dibromo-1-methylcyclohexyl 4-acetic acids; it reads:—"For purposes of classification, therefore, it is convenient to regard the dibromides as exhibiting two elements of asymmetry, namely, a centroasymmetry exhibited by the right-hand part of the configurations of Figs. 1, 2, and 3, and an asymmetry of the carbon atom (7), as is shown in Figs. 2 and 3."

There are many reasons why the classification suggested in this quotation should not be adopted, amongst them being the following:—

There is no centroasymmetry exhibited by the *right-hand* part of the configuration of Fig. 1, for if everything right of carbon atom (1) be included, the configuration is asymmetric about the plane of the ring. That the asymmetry of the *whole* of the configuration is traceable to the asymmetry of carbon atom (1) has been discussed above.

In Figs. 2 and 3 likewise, neither the *right-hand* nor the *whole* of the configurations show any asymmetry that is not traceable to carbon atom (7), and which is not destroyed when the asymmetry of that atom [carbon atom (7)] is destroyed.

Neither is it now possible to defend the system on the ground that it is but the counterpart of that by which many levorotatory compounds are designated dextro, by reason of their having been derived from a dextro-parent substance—and *vice versa*—for the parent substance (1-methylcyclohexylidene-4-acetic acid) cannot now be looked upon as being "centroasymmetric."

As mentioned above, in all these dibromo-compounds described by Perkin and Pope, and illustrated by them in

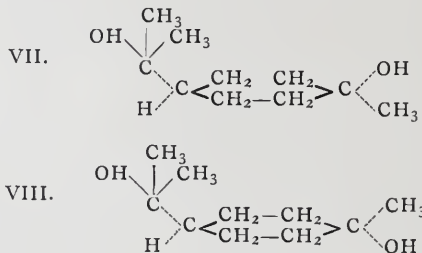
Figs. 2 and 6 (*loc. cit.*), the asymmetry of the molecule is traceable to the carbon atom (7) and disappears with it.

In reality these bromo-derivatives are merely cases of *cis*- and *trans*-isomerism of cyclic compounds through the first instance of the isolation of the different optical isomerides derived therefrom.

Thus, *cis*-terpin (VII.) and *trans*-terpin (VIII.) are quite similar instances of this, and, moreover, although neither of these can be said to be centroasymmetric, yet by replacement of one of the methyl groups in the system

$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}-\text{CH}_3 \\ \diagdown \\ \text{OH} \end{array}$ by another group (not OH), then there are pos-

sible exactly similar isomerides as those discussed above—*d*- and *l*-*cis* and *d*- and *l*-*trans*—yet here, also, the asymmetry is entirely traceable to the asymmetric carbon atom thus produced.



307. "Nitrites of the Alkylammonium Series. Part II. Propylammonium Nitrite and Butylammonium Nitrite and their Decomposition by Heat." By PRAFULLA CHANDRA RAY and JITENDRA NATH RAKSHIT.

Propylammonium nitrite decomposes when heated mainly into nitrogen, isopropyl alcohol, and water; small quantities of nitrosodipropylamine and in some cases nitric oxide and propylamine were also detected.

Butylammonium nitrite when heated decomposes into nitrogen and isobutyl alcohol.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 6th, 1911.

Mr. A. R. LING, Vice-President, in the Chair.

MESSRS. Ronald Devereux Carty, George Frederick Wesley Martin, and William Keighley Walton were elected members of the Society.

Certificates were read for the first time in favour of Miss Maud Gazdar, Fox Hall, Upminster, Essex; and Herbert Hawley, City Analyst's Laboratory, Council House, Birmingham.

Certificates were read for the second time in favour of Messrs. Shelton Gottlieb Agar, George Stephen Barton, Stanley W. Bridge, Richard Victor Briggs, Francis Clifford Dyche-Teague, Francis Archibald Mason, William Bristow Saville, and George Alfred Stokes.

The following papers were read and discussed:—

"Estimation of Small Quantities of Essential Oil in Spices, &c." (Part II.). By J. A. BROWN.

The paper is a continuation of the one on the same subject in the *Analyst* for September, 1910, and will give data along the same lines as the previous paper to show the applicability or otherwise of the dry distillation combustion process to the estimation of the essential oils in ginger, coriander, aniseed, cardamom, black pepper, pimento, bay, cedar, santal-wood, rosemary, eucalyptus, and juniper.

"Determination of Furfural by means of Fehling's Solution." By L. EYNON and J. H. LANE.

It is shown that under the conditions prescribed by

Flohil (*Analyst*, 1911, xxxvii., 161), the copper reducing power of furfural is not independent of concentration.

Tables are given showing the amounts of cuprous oxide obtained with different quantities of furfural.

The limit of error in the method described is about 3 or 4 per cent.

"*Examination of Petroleum Mixtures.*" By J. H. COSTE, E. T. SHELBURN, and E. R. ANDREWS.

The authors point out that the definitions of petroleum contained in the Petroleum Acts, 1871—1881, and in the Order in Council of 1907, necessitate in many cases a much more extended examination than the mere determination of flash-point.

They indicate methods of examination which have been found useful.

"*Note on Ground Almonds.*" By G. CECIL JONES and REGINALD F. EASTON.

Ground almonds having been reported as adulterated by addition of starchy material, it was represented to the authors that starch was a normal constituent of immature almonds.

It was, however, found easy to separate the starchy material mechanically and almost quantitatively, and to identify it as a wheat product.

"*Method for Determining the Amount of Insoluble Particles in Raw Rubber.*" By CLAYTON BEADLE and HENRY P. STEVENS.

The authors discuss the ordinary methods employed for estimating impurities by losses on washing, and point out the same are not applicable to rubbers of a higher degree of purity. They describe methods for removing the rubber substances by means of depolymerisation in solvents, such as nitrobenzene, high boiling petroleum, phenetol, &c., whereby the rubber is removed and the residue weighed.

A table is given of the mineral and organic constituents of several different kinds of rubbers, and figures showing diminution in impurities as the result of washing.

"*Note on the Determination of Small Quantities of Methyl Alcohol.*" By C. SIMMONDS.

Denigès' method for the detection of methyl alcohol (*Comptes Rendus*, 1910, cl., 832) may be advantageously applied to the quantitative determination of small proportions of this alcohol in such articles as medicinal tinctures.

Details are given of the procedure found suitable in such cases.

"*Note on Malefern.*" By ERNEST JOHN PARRY.

In this note the author draws attention to the almost universal adulteration of this drug, which is official in the British Pharmacopœia.

Twenty samples have been obtained from different sources in London, and found to contain large quantities of castor-oil up to 50 or 60 per cent.

Type samples of the drug have been prepared, and the author gives a number of standard figures with which the pure oil should conform. These include specific gravity, refractive index, saponification value, unsaponifiable matter, characters of fatty acids, determination of filicin.

These characters are quite sufficient to enable one to decide upon the purity or otherwise of a given sample.

"*Composition of Australian (Victoria) Milk.*" By E. HOLL MILLER.

The mean monthly composition of milk in Victoria from September, 1909, to August, 1910, is given in tabular form; the average percentage of fat is 4.15, and during the summer months (December to February) the solids not fat are very low, and this is ascribed to a flush of green herbage caused by copious rains.

The ratio between aldehyde figure and proteins, the rate of souring, and the composition of the ash practically agree with results found with English milk.

"*Composition of Sweetened Condensed Milk.*" By E. HOLL MILLER.

Tables are given showing the composition of fifteen

samples purchased in Victoria and New South Wales, representing condensed milk prepared in Australia.

Tyrosin was detected in nearly every sample; it makes its appearance in the third or fourth month from manufacture, and old samples show fairly large crystalline tufts.

"*The Aldehyde Figure of Butter.*" By E. HOLL MILLER.

Proteins may be rapidly determined in butter from the aldehyde figure; 10 grms. of butter are melted, and 25 cc. of water at about 65° C. stirred in, and the aldehyde figure determined as usual, the end-point being observed by allowing the contents of the beaker to settle and noting the colour of the aqueous layer.

NOTICES OF BOOKS.

The Advance of Photography; its History and Modern Applications. By A. E. GARRETT, B.Sc. Kegan Paul, Trench, Trübner, and Co., Ltd. 1911. (12s. 6d. net)

THIS is a volume of 382 pages with 167 illustrations upon the principle and general progress of photography. The subject, although treated in a scientific manner, is presented in such a way as to interest the general reader, and now that the practice of photography has become so universal the book will be welcomed by those who wish to master the principles that underlie one of the most fascinating pursuits of modern times. The first 72 pages are devoted to the history of the science from the early experiments of Wedgwood and Davy to the present time, and to the chemistry involved in the reactions, particular attention being paid to the important action of the compounds of chromium. This is followed by a chapter on lenses and the optical construction of the photographic combination, concluding with the practical results obtained by Cooke, Dallmeyer, and others in portrait and telephoto lenses. A series of half-tone plates is given, showing the effect of the introduction of "diffusion" into the otherwise sharp photographic image. Then follows a short chapter on camera appliances, which reads very like a collection of trade advertisements. The subject of the manufacture of the modern dry plate, including the preparation of plates sensitive to the visible spectrum, is exhaustively discussed. The section of micro-photography is complete and well illustrated, but unfortunately nearly all the plates bear the name of one of the prominent makers of this class of apparatus. This introduction of trade names largely pervades the whole book, and is to be regretted, as naturally it is unfair to those firms who have not been mentioned, and is not in conformity with the otherwise scientific character of the work. The book is well indexed, and has a table of contents.

The British Journal Photographic Almanac, 1912. 51st issue. Edited by GEORGE E. BROWN, F.I.C. 1434 pages. Crown octavo. London: Henry Greenwood and Co. (1s. net, paper, and 1s. 6d. net, cloth).

THE 1912 volume of the *British Journal Photographic Almanac* contains several new features which should add to the usefulness of this universal reference volume for photographers. Of these one should be of particular service to amateur workers. It is a series of articles in which, under the title "How to Do It," some 120 sketches are used to explain the exact way in which to go about such operations as mounting prints, copying, handling chemicals, making oil-prints, &c. Illustrated articles also deal fully with lantern-slide making and with at-home portraiture. In the pages devoted to the practical work of the year, all branches of photography are the subjects of articles on indoor and outdoor work, development, dark-room arrangements, printing processes, enlarging, and colour photography, whilst in another section all kinds of new apparatus for the photographer are described and illustrated.

Über Zerfallprozesse in der Natur. ("Decay Processes in Nature"). By Dr. C. ENGLER. Leipzig: S. Hirzel. 1911. (1.25 mk.).

In this pamphlet, which is a reproduction with some additions of a lecture delivered before the eighty-third meeting of the German Scientific and Medical Association at Karlsruhe, the author touches upon some of the problems of the day which are attracting the attention of the general public, as well as being systematically studied from many points of view by scientific men. Although he can necessarily do little more than give a mere outlined sketch of some of the problems he brings to the notice of his readers, he discusses them in a vivid and interesting style, and such questions as the origin of life and the utilisation of hitherto neglected sources of energy are quite briefly but adequately treated. Such lectures as these would provide excellent practice in reading for science students who wish to add to their knowledge of the German language.

Die Bedeutung der Kolloide für die Technik. ("The Importance of Colloids in Technology"). By Prof. Dr. KURT ARNDT. Second Edition. Dresden: Theodor Steinkopff. 1911. (1.50 Mk.).

This pamphlet was originally an amplification of a lecture delivered by the author, and subsequently published in the *Chemiker Zeitung*. The very favourable criticism given to the lecture induced the author to re-publish it in book form, and the rapid advance of the subject since the date of the first edition has led to the preparation of a new edition. In this it has been found necessary to make some few alterations and corrections and a large number of additions. Thus recent suggestions for the classification of colloids are noticed, and a section on suspension and emulsion colloids has been added, while other sections, such as those on the applications of colloidal chemistry in brewing and in mineralogy, have been very considerably enlarged.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 20, November 13, 1911.

Propagation of Light in Fluorescent Substances.—Jean Becquerel.—Burke has stated that the power of absorption of uranium glass increases when fluorescence is excited, and Nicholls and Merritt have constructed curves of "the absorption of fluorescence." The author has further investigated the question of the propagation of light during fluorescence, and has found that neither in rubies nor in emeralds does the fluorescent state modify appreciably the velocity of the propagation of radiations of the same period as the radiations emitted. A variation in the index of refraction of 10^{-6} , fifty times smaller than the variation due to absorption for the band 693.2μ of the ruby, would have been visible. It is, of course, impossible to say definitely that a smaller effect is not produced, but in the author's opinion the absorption of fluorescence probably does not exist.

New Hypotheses of Molecular State of Substances in Solution.—Pierre Girard and Victor Henri.—In Fouard's osmometric experiments it seems probable that the equilibrium observed does not correspond to an equality of the osmotic pressures of the solutions in question, but is the result of osmotic currents of electrostatic origin. Hence these experiments cannot be employed to prove the polymerisation of the molecules and the inapplicability of the theory of van't Hoff and Arrhenius. The osmotic pressure of saccharose measured by Morse corresponds exactly to the molecular weight 342, the cryoscopic lowering of acetic acid is the same as that of an isomolecular solution of sugar; hence the molecules of acetic

acid in aqueous solution are simple, and not double, molecules as Colson assumes.

Hypo-iodous Amides.—E. Boismenu.—The iodated amides, prepared by the action of nascent hypoiodous acid on amides, are hypoiodous amides. They are decomposed by water, they decolorise indigo, and act on a solution of potassium iodide, liberating double the weight of the iodine contained in their molecule. They are very unstable, and their instability increases as their molecular weight decreases.

Properties of Monobrominated Acrolein.—M. Lespiau.—Monobrominated acrolein can be prepared by the action of potassium acetate on acrolein dibromide. Analysis shows that the formula is $C_3H_4Br_2O$, and the molecular weight, determined in acetic acid, is 230, which is fairly close to the theoretical number 216. With a cooled solution of hydrazine it gives an energetic reaction, and crystals of pyrazol are formed. With HCN in presence of KCN it yields an unsaturated nitrile, which can readily be saponified by aqueous hydrochloric acid, the product being the acid $CH_2=CBr-CHOH-CO_2H$. Two atoms of bromine can be added to this acid, giving $CH_2Br-CBr_2-CHOH-CO_2H$. The author has also prepared the isomeric acid $CHBr_2-CHBr-CHOH-CO_2H$.

Metallic Alcoholates.—E. Charblay.—Alcoholates of calcium can be prepared either by double decomposition between calcium nitrate and an alkaline alcoholate in liquid ammonia, or by the action of calcium-ammonium on the corresponding alcohols. Similar methods can be applied to the preparation of alcoholates of barium and strontium. Well-defined alcoholates of lead can be obtained by the method of double decomposition. The methylate, ethylate, isobutylate, and amylate of lead are all white products, excessively sensitive to the action of heat and humidity.

Attempts to Prepare Tetrolic Aldehyde.—P. L. Viguier.—The author has tried to prepare tetrolic aldehyde by direct methods, but has as yet been unsuccessful. Thus none is formed by the action of diethylformamide on the bromide of allylene magnesium, nor when ethyl formate acts at a low temperature on allylene magnesium bromide. Sodium allylene acts on ethyl formate, and if water is added at once the smell of tetrolic aldehyde is plainly detected. But the reaction is never energetic and rapidly slackens in spite of shaking, and finally viscous products are obtained from which no aldehyde can be isolated.

Bulletin de la Société Chimique de France.

Vol. ix.—x., No. 22, 1911.

Salts and Ethers of Dithiocarbonic-alkylamino Acids.—E. Fourneau and M. Vila.—Phenylmethylthioazolonone can be prepared by mixing phenylmethylaminoacetate of ethyl with carbon disulphide and anhydrous ether. After some time crystals begin to form, and can be re-crystallised from alcohol. They are colourless and odourless, insoluble in ether, very slightly soluble in water, fairly soluble in boiling alcohol, and very soluble in acetone. They melt at 137° . From thiazolonone the following salts can be obtained:—Sodium phenylmethylaminoacetate dithiocarbonate of sodium, sodium phenylmethylaminoacetate dithiocarbonate of mercury, and potassium phenylmethylaminoacetate dithiocarbonate of antimony.

MEETINGS FOR THE WEEK.

THURSDAY, 28th.	} Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "The Childhood of Animals," by F. Chalmers Mitchell, LL.D., D.Sc., F.R.S.
SATURDAY, 30th.	

Royal Institution.—The Annual Christmas Course of Juvenile Lectures at the Royal Institution begins on Thursday next, December 28, at 3 o'clock, when Dr. P. Chalmers Mitchell will deliver the first of six lectures on "The Childhood of Animals."

THE CHEMICAL NEWS.

VOL. CIV., No. 2718.

NOTES ON THERMOSTATS AND DEVICES USED IN CONNECTION WITH THERMOSTATS.*

By ALEXANDER CHARLES CUMMING, D.Sc.

It is comparatively recently that the thermostat came into general use, and many improvements have been effected in the last few years. A collection has therefore been made of recent devices in the hope that a collection of the somewhat scattered notes on the subject may prove useful. In the preparation of these notes I am indebted to several of those named below for information in regard to various improvements and modifications.

The Thermostat.—Copper appears to be the most satisfactory material for a thermostat. Enamelled iron usually cracks and rusts after a short time, particularly if used at higher temperatures.

It is desirable that the thermostat should contain so much water that no appreciable alteration in temperature is effected when the experimental apparatus is introduced. The level of the water in the thermostat should be kept constant, and an apparatus for this purpose is figured in a paper by Lumsden (*Journ. Chem. Soc.*, 1902, lxxxi., 352). If the thermostat is near a water-tap, the level may be kept constant with the arrangement commonly used for hot water-baths.

Glass-fronted Thermostats.—Most of the German-made thermostats have the glass cemented into a groove in the metal. This gives a water-tight joint, but the cement is somewhat readily fractured. A more satisfactory method is the use of a strip of rubber between the glass and metal, the glass being clamped to a flange on the side of the bath. Several of this type are in use in Edinburgh and Aberdeen, and are much superior to those with cement (made by Fraser, 16, Haddon Street, Aberdeen).

Flow of Liquid at Constant Temperature.—A thermostat arranged to supply a stream of water at constant temperature is described by Lowry (*Trans. Faraday Soc.*, 1907, iii., 119).

Regulators.

Since the value of the thermostat depends on the constancy of the temperature, it is natural that many varieties of regulators should be described. In all modern forms, the expansion of a liquid is used to actuate a cut-off for the heat supply.

Choice of a Liquid.—The liquid to be used in the regulator should have a low specific heat, a high coefficient of expansion, and preferably a low density. As these are the main factors in the choice of a liquid, a few figures may be given for the specific heats and coefficients of expansion of some common liquids. The numbers are approximate, and refer to temperatures about 25°.

Liquid.	Increase in volume of 1 litre for 1° rise in temperature.	Specific heat.
	Cc.	
Water	0.25	1.0
40 per cent calcium chloride solution	0.5	0.63
Mercury	0.18	0.03
Benzene	1.2	0.4
Toluene	1.1	0.4
Ethyl alcohol	1.1	0.5
Ethyl ether	1.1	0.55
Chloroform	1.3	0.23
Carbon tetrachloride	1.1	0.2

The very low specific heat of mercury is counterbalanced by its great density, which necessitates the use of thick-walled apparatus. Most organic liquids show an expansion with temperature of the same order as those quoted, but

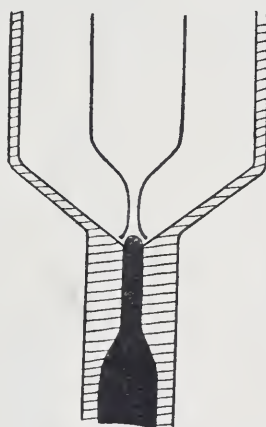


FIG. 1.

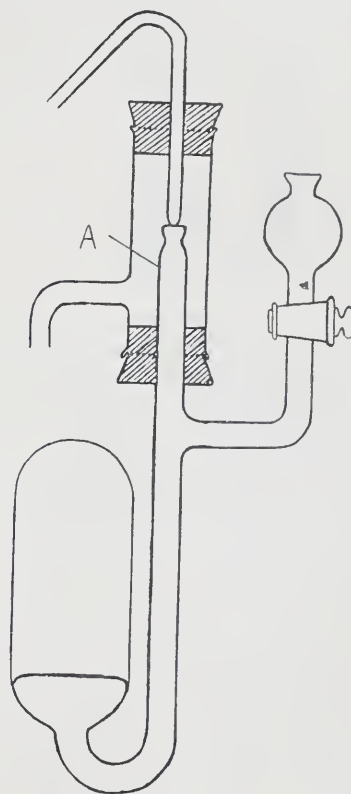


FIG. 2.

paraffin oils are much lower and are unsuitable. It is mainly a matter of convenience which of the above organic liquids is used, but that with the lowest density will be slightly more efficient than the others.

Bulb of Regulator.—The greater the surface exposed, the more sensitive will be the regulator; consequently, several have recommended the use of a spiral to contain the liquid (Gouy, *Journ. de Phys.*, 1897, [3], vi., 479, and others). Lowry has described a convenient form of spiral (*Trans. Chem. Soc.*, 1905, lxxxvii., 1030).

The sensitiveness of the regulator is increased by use of a metal spiral instead of glass, and a satisfactory connection can be made with rubber, if a water trap is introduced between mercury and the organic liquid, so that the water layer covers the junction between metal and glass.

Method of Cutting off the Gas Supply.—Two forms of "cut-off" with novel features may be mentioned. That

* A Paper read before the Faraday Society, December 6, 1911.

described by W. Heber Green (CHEMICAL NEWS, 1908, xcvi., 49) has been tried in the laboratory of the University of Edinburgh, and found to effect a considerable improve-

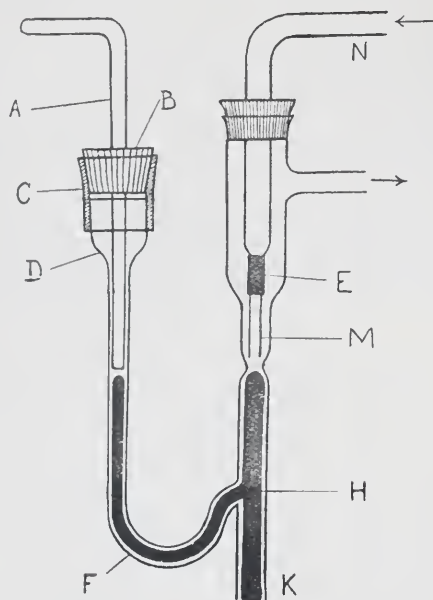


FIG. 3.

ment. The inlet tube for the gas is pushed down until almost touching the constriction in the outer tube, as shown in Fig. 1. The lower end of the inlet tube is opened out slightly, and the tendency of mercury to stick in the narrow tube is thus prevented. The regulator can be adjusted for any desired temperature by removal or addition of mercury through a side tube with glass tap (similar to arrangement shown in Fig. 2).

The apparatus shown in Fig. 2 was designed by T. S. Patterson (*Journ. Soc. Chem. Ind.*, 1902, xxii.), and its particular merit is that it prevents the formation of scum on the mercury surface. The top of the inner tube A, which is completely filled with mercury, is covered with a thin rubber sheet; the expansion of the liquid with rise of temperature presses this rubber against the inlet tube, and thus closes it. Dr. Patterson has used this type of regulator for ten years and finds it very satisfactory. One regulator with 80 cc. of benzene in the bulb has been used in the thermostat of a polarimeter, and no change could be detected with a Beckmann thermometer during a day or two.

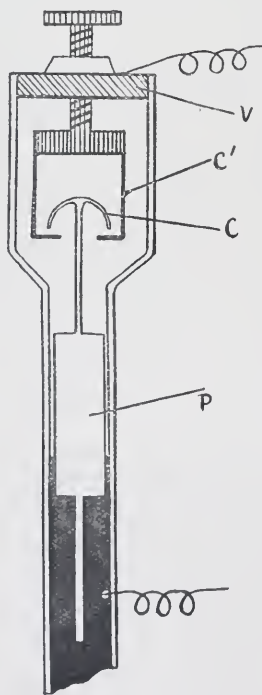


FIG. 4.

Adjustment for Alteration of Temperature.—The adjustment of the regulator for a different temperature is usually effected by removal or addition of mercury through a side tube, fitted with a glass tap. The ease of adjustment varies with the particular tap, and is sometimes troublesome.

A. Slator describes another method of altering the mercury level (*Journ. Soc. Chem. Ind.*, 1911, xxx., 61). Fig. 3 shows the upper part of the regulator, and does not include the toluene bulb. The glass rod plunger, A, passes through the rubber bung, B, and forces the desired amount of mercury into the stem, K, of the apparatus. The cup, D, is filled to the exclusion of all air by a mixture of about two parts glycerin and one of water. The bung, B, rests on the cup, and is held in position by the rubber tubing, C, which overlaps the bung and the cup. The plunger readily slides through the bung owing to the efficient lubrication by the glycerin and water, and to the fact that the tubing, C, whilst making a tight joint, does not unduly compress the bung. The bend, F, ensures the mercury remaining in the side piece, even if the level in the stem falls below the joint, H. By means of this arrangement the regulator can be adjusted accurately to any desired

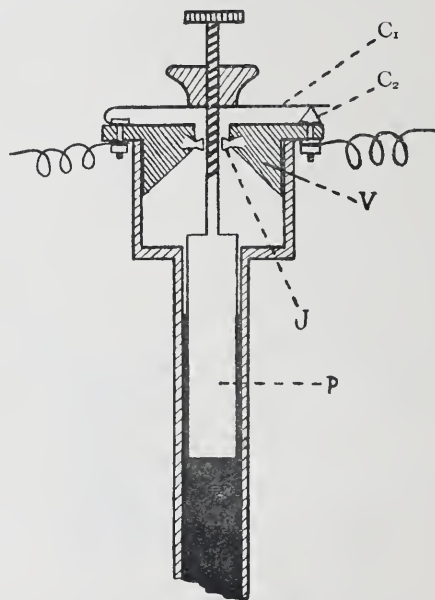


FIG. 5.

temperature over a wide range of temperatures. It has also been noticed that the fragile end, M, of the tube, N, is rendered less liable to breakage if the two are connected by means of narrow rubber tubing, E (bicycle valve tubing), instead of being rigidly attached.

Electrically controlled Thermostats with Gas Heating.—W. Meyerhoffer described a thermostat in which the bulb of the regulator was filled with mercury (*Zeit. Phys. Chem.*, 1890, v., 99). An electrical device was used to cut off the gas supply by pressure on a rubber tube, whenever the circuit was closed by expansion of the mercury.

Another electrically controlled thermostat is described by J. L. R. Morgan (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 344), which may be used at any temperature between 0° and 90°. The bath liquid is heated or cooled by a regulated supply of hotter or colder liquid. It is claimed that this thermostat is very satisfactory in use.

Electrically Heated Thermostats.—This subject is being dealt with at the same meeting by Prof. Hugh Marshall ("Notes on Thermostats," CHEMICAL NEWS, civ., p. 295), and the following notes are therefore intended only as an

addendum to his paper. It may be mentioned that a similar system of electric heating is described by J. and G. Gibson (*Proc. Roy. Soc. Edinburgh*, 1909, xxx., 255), which differs in some details. A full description with diagrams of their apparatus is given in the above-mentioned paper.

Some time ago, on account of lamps breaking, I tried heating with naked platinum wire, the other arrangements being as described by Prof. Marshall. So far as a brief trial showed, this method of heating appears satisfactory. It may be mentioned that if bare wires are used for heating, they must be joined at the ends to thick wires to seal into the glass, as glass is immediately fractured by the heat from a thin wire.

Thermostat with several Novel Features.—G. A. Hulett uses a thermostat in which about 100 litres of kerosene (paraffin oil) serve as the bath liquid (*Phys. Review*, 1911, xxii., 276). This was kept dry by a dish of calcium chloride in the bath. The regulator is a toluene regulator with several long narrow limbs, and the regulation is electrically controlled.

The heating coils consist of 0.25 mm. nickel wire wound on 10 mm. glass tubes. The tubes were shellacked to hold the wire in place, and it was found that the shellac was unaffected by the oil in the bath. The resistance of the coil was about 120 ohms, and the 110-volt circuit was used, with an external resistance to reduce the current. It was found that about 0.4 ampère was sufficient to control the bath.

New Electrically-controlled Regulators.—I am indebted to Mr. Charles Fraser for a description of these regulators, which have not been previously described.

In the first form, Fig. 4, a metal plunger, P, floats on the surface of the mercury. This carries a curved platinum wire, c, at the end of a rod, and contact is made when c comes in contact with c', the point of contact on c' being also covered with platinum. The vulcanite plug, v, serves to insulate c' and its connections. The rough adjustment is effected by alteration of the amount of mercury in the usual way, while the final adjustment is effected by raising or lowering c' by means of the brass screw and mill-head.

The particular advantage of this regulator is that contact is made and broken between platinum contacts, and the splashing of mercury, due to sparking, is thus avoided. Dr. Knox has used one of these regulators for many months, and found it extremely satisfactory and reliable.

The second form, Fig. 5, is interesting in that no current passes through the mercury. Contact is made between two platinum terminals, c₁ and c₂, and broken when the rise of the plunger lifts c₁. Any side-to-side movement of the plunger and connections is prevented by the garnet jewel setting, j, in the vulcanite ring, v. The regulating screw serves for fine adjustment, the rough adjustment being effected as usual by alteration of the amount of mercury in the regulator. Mr. Fraser regards this form as an improvement on the first form.

Shaking and Stirring Apparatus.

Shaking Apparatus.—The type which is in general use is described by von Ende, who gives a photograph of the apparatus (*Zeit. Anorg. Chem.*, 1901, xxvi., 129). It is desirable that the movable bar by which the bottles are held in place should be made of wood, as with a metal bar there is more risk of fracture,

Dr. J. Knox has shown me a neat device for a driving band to be used under water. Leather and gut bands both disintegrate in water, particularly at high temperatures, and Dr. Knox therefore uses a band made of brass wire wound in a close narrow spiral. The advantages of this are obvious.

Stirring.—Efficient and vigorous stirring is necessary if the temperature fluctuations are to be kept small. Personally I like a glass "angle" stirrer of the type shown in Fig. 6. The side tube is about 2 inches long, and the vertical tube of such length that it ends about 1 inch from the bottom of the bath when the side tube is about 2 inches below the surface. This gives a good circulation of water.

For some time I have stirred a deep thermostat by blowing through a stream of air so that the air-bubbles ascend through a wide tube which is open at both ends. This causes a constant circulation of the water. The temperature at one level has not been found to vary more than $\pm 0.05^\circ$, and the maximum variation noticed in different corners of the bath was 0.1° , but it is usually rather less. For many purposes this is sufficient, and it is sometimes more convenient to use an air-blower than a mechanical stirrer. For closer constancy, however, a much more vigorous stirrer is necessary.

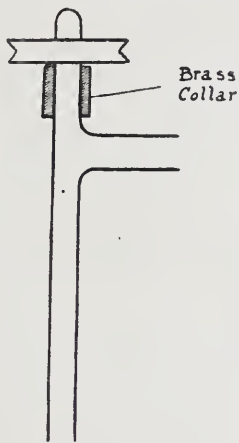


FIG. 6.

THE SOLUTION VOLUMES OF NITRIC ACID.

By V. H. VELEY, F.R.S.

ATTENTION has been drawn within recent years by the investigations of Bousfield and Lowry to *solution volumes* (*Phil. Trans.*, 1905, A, 204, 253; *Trans. Far. Soc.*, 1910, v., 407), namely, the volumes occupied by 1 grm. of solute under different conditions of concentration and temperature. By this conception there are studied the effects produced by such variations on the *solute* only instead of, as heretofore, on the *solute* and *solvent*, taken conjointly, in the form of the resulting contractions.

Further, it is now generally held that liquid water is a ternary mixture of trihydrol, H_6O_3 , dihydrol, H_4O_2 , and monohydrol, H_2O , the relative proportions of which vary with the temperature. (For the arguments in favour of this hypothesis reference may be made to the general discussion on the constitution of water, *Trans. Far. Soc.*, 1910, v., 393—445). When, therefore, a solute is added to water two events may occur: *firstly*, the solute may break up the more complex hydrol molecules, and *secondly*, the solute may combine with the resolved molecules to form hydrates, the second event, if it occurs, following immediately upon the first. In the case of certain metallic and ammonium salts the first event only occurs, but in the case of other salts, as also of the stronger acids and bases, both events take place, so that at certain concentrations a condition of equilibrium may be set up between water and solute, on the one hand, and the hydrate of the solute on the other.

From a study of certain physical properties of nitric acid, namely, electric conductivity, refractive indices, densities, and contractions, Manley and the author (*Phil. Trans.*, 1898, A, 191, 365; *Proc. Roy. Soc.*, 1902, lxi., 86; *Journ. Chem. Soc.*, 1903, lxxxiii., 1015; *Journ. Soc. Chem. Indust.*, 1903, 223, &c.), found alterations, more or less defined, at concentrations approximately coincident with the composition of certain hydrates, all of which had been noted by previous workers. It does not appear to be necessary to recapitulate the evidence, though it might be worth while to allude to a criticism to the effect that "the more carefully work of this type is conducted, the greater number of hydrates discoverable." Such a criticism can hardly be taken seriously, as, clearly, it would be subversive of all careful work in any branch of science if it

were held that greater care did not lead to greater knowledge.

But besides the discontinuities corresponding to the formation of hydrates, there is a well-marked point of alteration for all physical properties at a concentration of about 95 per cent, to which attention had not previously been drawn; in this respect nitric resembles sulphuric acid. The view was formerly held that the two cases were similar, in that as sulphuric acid of 96 to 100 per cent contains H_2SO_4 and SO_3 molecules, so nitric acid of like concentration contains HNO_3 and N_2O_5 molecules. But it now appears that in the case of the latter, if not of both, the hypothesis of associated molecules $n\text{HNO}_3$ and $n\text{H}_2\text{SO}_4$, analogous to $n\text{H}_2\text{O}$, is more probable.

For the purpose of calculating out the solution volumes of nitric acid the determinations are utilised, which were made by the author of the densities at different concentrations, and at the three temperatures 4° , 14.2° , and 24.2° (in terms of water of 4°); most of these are reproduced in the "Physikalisch Chemische Tabellen" (Auflage iii., p. 325, Berlin, 1905) of Landoldt-Börnstein-Meyerhoffer.

It should be noted that the concentrations were determined by volumetric analysis, since stock solutions of 100 per cent nitric acid can only be prepared with difficulty, and, when so prepared, cannot be kept for a long time; it is therefore admitted that such results are not of the order of accuracy obtainable in cases in which a substance can be weighed with an error of a few decimilligrams. There is, also, the further weak point that, whereas the errors of volumetric analysis may amount even in favourable circumstances to as much as 1 in 400 parts, the errors of density determinations may amount to as little as 1 in 40,000 parts. A comparison of solution volumes as regards temperature is also restricted by the instability of concentrated nitric acid at temperatures above 25° , thus preventing determinations of any degree of exactness.

The determinations at $14.2/4^\circ$ and $24.2/4^\circ$ were recalculated in terms of $14.2/14.2^\circ$ and $24.2/24.2^\circ$ respectively, taking the density of water at $14.2^\circ = 0.99926$ and at $24.2^\circ = 0.99727$ (Thiesen, Scheel, and Disselhorst's "Tabellen," p. 13). For the purpose of an outline the densities for each difference of 10 per cent were calculated by interpolation on the assumption that within slight differences the density is a linear function of the concentration. From the figures thus obtained the solution volumes were calculated out by means of the formula—

$$(100 - p) V + p V_1 = \frac{100}{D}$$

in which V are the volumes of water at the three different temperatures, taken from Scheel's tables, V_1 the required solution volumes of nitric acid, D the densities, as calculated, and p the percentage concentrations.

The results are given in Table I., and the successive differences for each 10 per cent in Table II.

On inspection of the figures in Table II. it is evident that (1) the greatest increase occurs between 0 and 10 per cent, in round figures two-thirds of the whole, (2) the increase from 10 to 50 per cent is comparatively small, and (3) that between 50 and 100 per cent is more rapid and uniform with a slight falling off at the last figure.

The 50 per cent point corresponds very approximately with that of maximum contraction, which occurs at 53–54 per cent (as originally observed by Kolb, *Ann. Chem. Phys.*, 1867, [4], x., 140, and confirmed by Manley and the author), which corresponds to the composition of the hydrate $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$. The slight falling off at 100 per cent is in accordance with the variation noted in the text above.

The two limits of concentration which appear to call for more especial consideration are from 0 to 10 per cent on the one hand, and from 90 to 100 per cent on the other; intermediate points were selected, namely, 4.68 and 7.9 per cent for the former, and for the latter 94.04 and 98.07 per cent respectively. The solution volumes and the successive differences are given in Tables III. and IV. similarly as in the two previous tables.

TABLE I.—Solution Volumes of 1 Grm. Nitric Acid.

Per cent.	Temperature.		
	4° .	14.2° .	24.2° .
10	0.4370	0.4491	0.4727
20	0.4523	0.4638	0.4786
30	0.4626	0.4776	0.4913
40	0.4760	0.4942	0.5070
50	0.5044	0.5164	0.5257
60	0.5343	0.5447	0.5553
70	0.5631	0.5755	0.5847
80	0.5945	0.6037	0.6138
90	0.6268	0.6329	0.6381
100	0.6484	0.6564	0.6631

TABLE II.—Successive Differences for each 10 per cent.

10	0.4370	0.4491	0.4727
20	0.0153	0.0142	0.0069
30	0.0103	0.0138	0.0127
40	0.0124	0.0166	0.0157
50	0.0284	0.0222	0.0187
60	0.0299	0.0283	0.0298
70	0.0288	0.0309	0.0291
80	0.0314	0.0278	0.0271
90	0.0323	0.0292	0.0263
100	0.0216	0.0215	0.0250

TABLE III.—Solution Volumes of 1 Grm. Nitric Acid.

4.68	0.4342	0.4536	0.4693
7.9	0.4375	0.4506	0.4721
10	0.4370	0.4491	0.4727
90	0.6268	0.6329	0.6381
94.04	0.6364	0.6443	0.6523
98.07	0.6445	0.6535	0.6601
100	0.6484	0.6564	0.6631

TABLE IV.—Successive Differences.

4.68	+ 0.4342	+ 0.4536	+ 0.4693
7.9	+ 0.0033	— 0.0030	+ 0.0028
10	— 0.0005	— 0.0015	+ 0.0006
90	—	—	—
94.04	+ 0.0096	+ 0.0114	+ 0.0142
98.07	+ 0.0081	+ 0.0101	+ 0.0078
100	+ 0.0039	+ 0.0029	+ 0.0030

TABLE V.—Solution Volumes of 1 Grm. Nitric Acid.

Per cent.	Temperature, 15° .
4.6	0.4442
7.26	0.4472
10	0.4463

TABLE VI. Successive Differences.

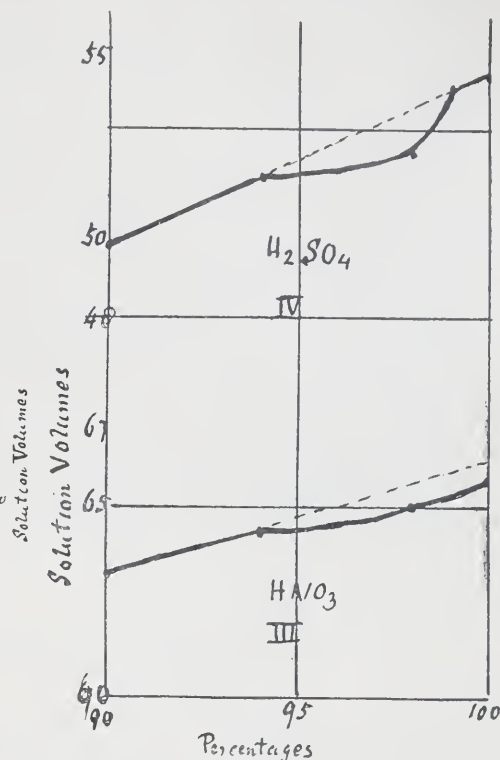
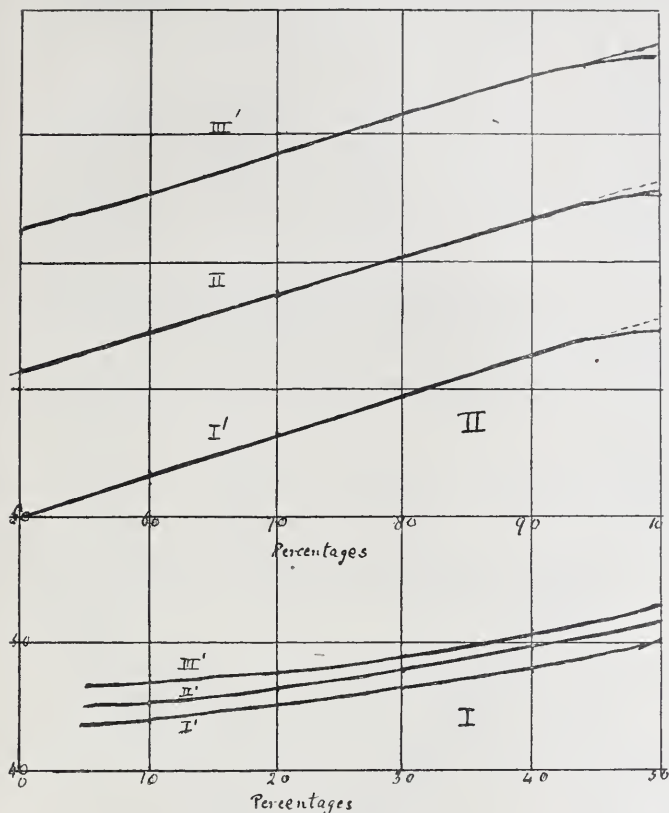
4.6	0.4442
7.26	+ 0.0030
10	— 0.0009

TABLE VII.—Solution Volumes of 1 Grm. Sulphuric Acid.

4	0.3375
7	0.3480
10	0.3480
90	0.4993
94	0.5160
98	0.5246
100	0.5447

TABLE VIII.—Successive Differences.

4	0.3375
7	0.0105
10	0
90	—
94	0.0167
98	0.0086
100	0.0201



It will be noted that the differences between the limits 4 and 10 per cent are very small, and almost within the limits of experimental errors, and as it was thought possible that there might be such errors, Lunge's density determinations at 15³/₄ for similar concentrations were calculated out according to the methods described above; the results are given in Tables V. and VI.

The values of the successive differences in the two sets of data are practically identical, and it would follow that the initial rapid increase in the value of the solution volumes takes place between 0 and 4 per cent. Previous observers have called attention to a slight variation of physical properties at the latter concentration, but no stress has been laid upon this point, mainly because most persons are sceptic as to the existence of hydrates containing a large number of water molecules; further, the complex nature of the molecules of liquid water was not realised.

As to the second limit of concentration, namely, 90 to 100 per cent, the successive differences gradually decrease, that between 98 and 100 per cent being the most apparent. To make the results clearer, they are set out in graphs I and 2, percentages being taken as abscissæ and solution volumes as ordinates. For each of the three temperatures 4°, 14.2°, and 24.2°, these graphs are divided into two sections, the three lower for concentration limits 4 to 50 per cent, and the three higher for 50 to 100 per cent; the origin of co-ordinates for the three latter is shifted in each case for the purpose of avoiding overlaps.

It is thus evident that the values from 4 to 50 per cent lie upon hyperbolic curves with the lower extremity flattened, and the values from 50 to 94 per cent lie upon straight lines; and, lastly, those from 94 to 100 per cent lie upon a curve, with the upper extremity flattened.

The probable explanation of the rapid increase in the

solution volumes from 0 to 4 per cent is that the addition of the nitric acid causes a resolution of the trihydrol and dihydrol molecules, which becomes nearly complete at a concentration of 4 per cent, from which point hydration commences; or possibly only the trihydrol molecules are resolved, and the curved portion from 10 to 50 per cent may result from the resolution of the dihydrol molecules and the formation of hydrates taking place in rapid succession.

As stated above, the results from 94 to 100 per cent are probably due to the production of complex molecules of nitric acid.

Comparison with Sulphuric Acid.—As sulphuric acid resembles nitric acid in the relations of certain physical properties, the solution volumes of the former were calculated between the same concentration limits of 0 to 10 and 90 to 100 per cent. For this purpose the density values of Domke and Bein ("Tabellen," p. 116), being those recalculated from the original observations of these authors ("Kaiserliche Normal-Eichungs Kommission," Heft 5, Berlin, 1904), were utilised, the values of 15/15 being selected.

The data of the solution volumes and successive differences are given in Tables VII. and VIII., as comparable with the previous tables.

As regards the lower limit, it is apparent that (1) the increase in solution volume is very great between 0 and 4 per cent, amounting to, in round figures, three-fifths of the whole; (2) the values at 7 and 10 per cent are, as in the case of nitric acid, identical. As to the upper limit, the irregularity is of different type, the values for 90, 94 (99), and 100 per cent being approximately linear functions of the concentration. The similarity and difference of sulphuric and nitric acid are rendered apparent by the graphs

3 and 4, drawn as the former graphs but on a more extended scale.

Bousfield and Lowry (*cf. supra*), in discussing their results obtained with sodium hydroxide, remark that the most complex solution is water, and the greatest simplification is reached with a 50 per cent solution of the base, which is about the limit of its solubility. The results with nitric acid show equally that the greatest simplicity is likewise reached at about 50 per cent, and remains constant up to about 94 per cent concentration; those of both nitric and sulphuric acids also show that the most complex solutions are, on the one hand, water, and on the other the acids themselves. The causes of these phenomena are, in all probability, identical, namely, the presence of polymeric or associated molecules.

There is, of course, the great point of difference between sodium hydroxide and the two acids in question, that whereas the former is an electrolytic conductor when fused and anhydrous, both the latter when free from water are conductors of a low order, and doubtless, if prepared and examined in vessels made of materials other than glass, might turn out to be perfect non-conductors.

The author proposes to study the densities of dilute solutions of certain metallic salts, which can be weighed out with accuracy, in order to determine whether there are irregularities of a similar type to those observed in the case of solutes discussed in the present communication.

A NEW FUNNEL. (THIRD COMMUNICATION).

By PHILIP BLACKMAN.

THE funnel in appearance is like the body of an ordinary funnel; that is, as if the stem and the adjacent part were cut away from a plain funnel. When a filter-paper is placed within this funnel a great part of the filter-cone, all or nearly all that portion containing precipitate or liquid, protrudes through the opening, A B, and is suspended, thus offering no contact with the funnel or other surface, and therefore affording perfect and accelerated filtration.

A small filter-paper should not be used with a large-sized (A to B) funnel to avoid the filter-paper slipping through.

This funnel, unlike the one described in Parts I. and II. (see CHEMICAL NEWS, vol. civ., pp. 30 and 211), owing to the absence of the stem and cone apex cannot be used with a narrow-necked or narrow-mouthed vessel; but this difficulty can be very easily overcome by placing it within an ordinary funnel (whether the latter is larger or smaller is immaterial so long as the part A to B rests within it) without in the slightest impairing its effectiveness. This aid is quite unnecessary when the diameter of the mouth of the receiving vessel is greater than that of the opening, A B. In quantitative work, where the filtrate is of importance, it is advisable after the filtration to wash down the outside of the opening, A B, adding the washings to the filtrate. These two insignificant disadvantages (which are absent from the funnel described in Part II.) are more than compensated by the simplicity of the funnel and its comparative low price.

This funnel cannot be made from an ordinary funnel by cutting off the stem and part of the body, for the simple reason that the sharp edge of the outlet, A B, will very quickly fray and cut through a moistened filter-paper, rendering a filtering operation impossible.

This funnel in various sizes is manufactured and supplied by Messrs. Townson and Mercer, 34, Camomile Street, London, E.C.

Experiments.

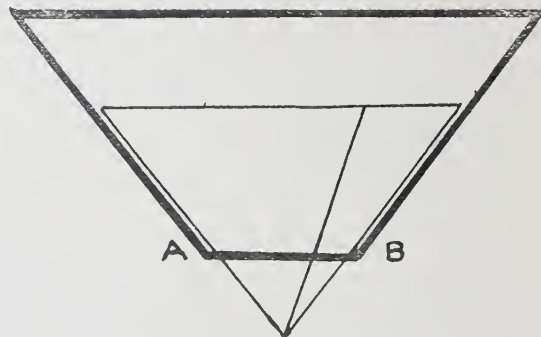
I. In each case water was passed through the filter, and the time was measured to collect 1000 cc., the water being

maintained continuously to within half an inch of the filter-edge.

Kind of funnel.	Size A—B (ins.).	Time (mins.).	Efficiency.
Plain	—	68	1.0
Blackman	I	38	1.8
	1 1/4	34	2.0
	1 1/2	28	2.4
	1 3/4	24	2.8
	2	20	3.4
	2 1/2	17	4.0

II. The quantities of water (cc.) were measured which were collected in sixty minutes, the water in each test being kept to within half an inch of the filter-edge.

Kind of funnel.	Size A—B (ins.).	Water (cc.).	Efficiency.
Plain	—	940	1.0
Blackman	I	1710	1.8
	1 1/4	1905	2.0
	1 1/2	2365	2.3
	1 3/4	2695	2.7
	2	3065	3.2
	2 1/2	3805	4.0



III. 0.5 gm. of finely powdered calcium carbonate was put into each filter-paper, and the time taken to collect 1000 cc. of water was measured, the water in each being continually kept to within half an inch of the filter-edge.

Kind of funnel.	Size A—B (ins.).	Time (mins.).	Efficiency.
Plain	—	250	1.0
Blackman	I	58	4.3
	1 1/4	50	5.0
	1 1/2	45	5.5
	1 3/4	38	6.6
	2	30	8.3
	2 1/2	25	10.0

IV. Using the filter contents of Experiment III., the volume of water passed through in sixty minutes in each case was measured, the water being always kept to within half an inch of the filter-edge.

Kind of funnel.	Size A—B (ins.).	Cc. of water.	Efficiency.
Plain	—	255	1.0
Blackman	I	1125	4.4
	1 1/4	1310	5.1
	1 1/2	1435	5.6
	1 3/4	1685	6.6
	2	2200	8.6
	2 1/2	2675	10.1

33A, Princess May Road,
Stoke Newington, London, N.

BURBANK'S SPINELESS PRICKLY PEAR.

"SANTA ROSA" (FICUS INDICA CLASS).

By E. V. FLACK, Government Analyst.

QUITE recently an analysis was undertaken of the above variety of prickly pear, grown from cuttings imported from California in 1909 by Mr. R. J. King, of Grahamstown.

The plants were grown without irrigation in a sandy loam soil on a hill slope. In two years the plants grew five feet, and some of the leaves weighed $7\frac{1}{2}$ lbs. The leaves are a glossy green, free from bristles, but have a few slender spines here and there, which are easily brushed off by the hand, and would in no way be an inconvenience to the feeding of stock.

The following are the results of the analysis of an average sample of four leaves weighing $11\frac{1}{4}$ lbs. Appended for comparison are the results of analysis of one leaf by Prof. Jaffa, of the State University of California, and of the common prickly pear of South Africa, *Opuntia tuna*, L. (Senior Analyst's Report, 1898).

	Spineless (Grahamstown).	Spineless (California).	Spiny (South Africa).
	Per cent.	Per cent.	Per cent.
Moisture . . .	92.25	94.70	91.36
Proteins . . .	0.61	0.66	0.39
Fat . . .	0.14	0.05	4.80
Carbohydrates . .	4.31	2.88	
Crude fibre . . .	1.22	0.75	2.18
Ash . . .	1.47	0.96	1.27
Silica . . .	0.031	—	0.036

It will be seen that the figure for moisture is somewhat lower in the Grahamstown grown plant; this is accounted for by the fact that the cuttings had been wilted in the sun for a period of three days before being received for analysis.

Government Analytical Laboratory,
Department of Agriculture, Grahamstown.

THE EFFECT OF CONTINUED GRINDING
ON WATER OF CRYSTALLISATION.

By C. E. GILLETTE.

BLEEKER (CHEMICAL NEWS, ci., 30) conducted a series of experiments to show the effect of long grinding on water of crystallisation. Some of the results were rather surprising, and we decided to repeat the work, and also to include a larger number of hydrates in the experiments. The conditions under which the work was done were as nearly uniform as possible. After grinding, the specimens were kept from the air in ground glass stoppered bottles of about 20 cc. capacity. Grm. portions were weighed out for all the determinations. In finding the water content of the unground specimens, the coarse crystals were merely crushed, and the fine crystals were used without further division. Usually about 3 grms. were taken for the grinding, which was effected in a large highly polished agate mortar. The grinding was continued for two hours. In some cases it might be difficult to decide whether the loss of water is due to efflorescence or to the heat caused by the continued grinding. Both causes doubtless contributed to some of the results.

In our work on barium chloride, the chemically pure products of two manufacturers were used. The sample was taken from the original package, and the amount of water determined, and another portion was ground two hours, and the water content estimated in the same way. The two specimens were then crystallised once from water, and coarse and fine crystals were obtained. They were dried between filter-papers, and at once placed in the glass stoppered bottles. The water was determined as in the original specimens. The results are as follows:—

		Crystals.	
Per cent.		Coarse (per cent).	Fine (per cent).
<i>Kalbaum's.</i>			
Unground ..	15.03	14.86	14.84
Ground ..	14.79	14.80	14.80
Loss ..	0.24	0.06	0.04
<i>Merck's.</i>			
Unground ..	14.89	14.78	14.78
Ground ..	14.38	14.74	14.77
Loss ..	0.51	0.04	0.01

It will be noticed that the loss is greater in the original substance than after one crystallisation from water. It is also greater in the coarse than in the fine crystals. The increase in weight, and the stickiness noticed by Bleeker in the case of barium chloride, were probably due to the presence of the very deliquescent calcium chloride as an impurity.

To ascertain whether it was superficial water that the grinding removed, or the water of crystallisation, portions of one of the original specimens, and of the coarse and fine crystallisations, were weighed out, heated a few moments, and the loss of water determined. The residue was then ground for two hours, and portions weighed out and again heated, and the loss by the grinding determined. The results were as follows:—

	First deter- mination (per cent).	Second deter- mination (per cent).
<i>Original Specimen, 14.89 per cent Water.</i>		
Removed by first heating . .	2.31	14.62
Removed by second heating . .	12.42	0.26
Total . . .	14.73	14.88
Loss . . .	0.16	0.01
<i>Purified Crystals, 14.78 per cent Water.</i>		
Removed by first heating . .	4.75	14.11
Removed by second heating . .	10.01	0.68
Total . . .	14.76	14.79
Loss . . .	0.02	0.01

It requires a comparatively low temperature to remove 10 or 12 per cent of water. It was also observed that the specimen in the crucible could be placed very near the flame without decomposition. Results that differed from one another by no more than one-hundredth of a per cent were easily attainable. The results with barium chloride seem to indicate that most of the water removed by grinding is superficial, although a small portion of the water of crystallisation can also be removed.

To learn the effect of the atmosphere upon barium chloride before and after grinding, portions of each were left in the air a few days. The unground specimens underwent no change, but the ground portions took up the greater part of the water that had been removed. The fine crystals after grinding would take up slightly more water than the coarse ones.

Removed by grinding (per cent).	Days in air.	Regained (per cent).	Kind of crystals.
0.04	1	0.007	Fine.
0.04	3	0.03	Fine.
0.06	1	0.01	Coarse.
0.06	3	0.04	Coarse.
0.24	1	0.06	Uncrystallised.
0.24	3	0.16	Uncrystallised.

Potassium Alum, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.
Ammonium Alum, $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

These salts require more care in heating than barium chloride, as they are quite easily decomposed. The commercial products were purified by crystallisation, and

coarse and fine crystals were obtained. The water was determined in both ground and unground portions. The grinding could not be carried on in a porcelain mortar on account of the tendency to cling to the sides of the dish. The portion for the determination was placed as nearly as possible in the centre of the crucible, where it fused to a round ball, thus avoiding the tendency to creep over the sides. The tests failed to show any decomposition of the salts by the heating. The water was also determined in an air-bath at a temperature of 105–110°, but equally good results were attainable in the ordinary way.

	Coarse (per cent).	Fine (per cent).
$\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.		
Unground	47'13	46'98
Ground.. ..	44'60	44'75
Loss	2'53	2'23
$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.		
Unground	45'48	45'44
Ground.. ..	42'97	43'42
Loss	2'51	2'02

Strontium Chloride, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.

Only a small quantity of the water is removed at a low temperature. It decomposes more easily than barium chloride, and the heating must be longer continued and at a lower temperature.

	Uncrystallised (per cent.)	Crystallised.	
		Coarse (per cent.)	Fine (per cent.)
Unground ..	39'94	40'41	39'63
Ground ..	38'92	38'42	38'10
Loss ..	1'02	1'99	1'53

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

This salt is quite efflorescent, and as the specimen at hand had been in contact with the atmosphere for some time, no determination was made before crystallising. The work was pushed as rapidly as possible before any change in the crystals could take place. A part of the loss is undoubtedly due to efflorescence.

	Coarse (per cent.)	Fine (per cent.)
Unground	42'39	42'15
Ground.. ..	38'66	38'82
Loss	3'73	3'33

Disodium Phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

This salt was the most difficult to handle of any of the series. After grinding for about an hour, it became pasty, adhering quite firmly to the sides of the agate mortar. If constantly scraped loose, it soon becomes a dry powder again. It was difficult to secure uniform results, owing, no doubt, to the effect of atmospheric changes upon the crystals. The results given, which seem somewhat erratic and surprisingly high, are considered a fair sample of those obtained.

	Original sample (per cent.)	Crystallised.	
		Coarse (per cent.)	Fine (per cent.)
Unground ..	61'13	62'45	60'67
Ground ..	33'21	32'35	32'01
Loss ..	27'94	30'10	28'66

Manganese Chloride, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.

A very pure specimen of the salt (Kahlbaum's) was at hand. No attempt was made to crystallise it, as the number of molecules of water of crystallisation it may contain depends upon the temperature. The crystals became pure white when ground.

	Per cent.
Unground	34'03
Ground	32'11
Loss	1'92

I desire to express my hearty thanks to Dr. N. Knight for help and suggestions in carrying on this work.

Cornell College, December 5, 1911.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7th, 1911.

Dr. M. ONSLOW FORSTER, D.Sc., Ph.D., F.R.S.,
Vice-President, in the Chair.

MR. F. Thomas was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Hilmar Johannes Backer, D.Chem., 4, Upper Bedford Place, W.C.; Ernest Arthur Bearder, M.Sc., Mayfield, Wythenshawe Road, Sale; Gibbs Blackstock, B.A., 79, Prince Arthur Avenue, Toronto; Frederic Fernandez Curtis, 20, Bury Street, Bloomsbury, W.C.; Rowland Holliday Ellis, Hope Cottage, Brayton Road, Selby; Thomas Sidney Haines, 73, Kennington Avenue, Bristol; William McMillan, 72, Wellington Street, Greenock; Ernest Meyer Myers, care of The Shelton Iron, Steel, and Coal Co., Ltd., Stoke-on-Trent; William Johnson Smith Naulton, B.A., B.Sc., 1, New Street, Woodbridge; James Pettigrew Ogilvie, Homedale, Hendon Lane, Finchley, N.; William Raitt, Dehra Dun, N.P., India; Walter Morrell Roberts, M.Sc., The Cedars, Whalley Range, Manchester; Bertram James Smart, B.Sc., Testing Office, Lithgow, N.S.W.; Cecil Hamersley Waldron, 28, Hungerford Road, Camden Road, N.; John Charles Withers, Ph.D., 83, Edgeley Road, Clapham, S.W.

A ballot for the election of Fellows was held, and the following were declared duly elected:—Arthur Cecil Bescoby, B.A.; Bertram Alfred Bull; Joseph Beauchamp Bull; Edwin Johnson Charlton, M.Sc.; Barun Chandra Dutt, M.A.; Charles Christian Gardthausen; John Henry Garner, B.Sc.; Arthur Josiah Hoffmeister Gauge; Rufus Gaunt, M.Sc., Ph.D.; Sydney Hall, B.Sc.; James Hogan Hill; Cyril Vincent Hodgson; Henry James Hodson, M.Sc.; Alexander Frederick Hogg, M.A.; Sant Ram Khosla; Harold King, M.Sc.; Geoffrey Martin, M.Sc., Ph.D.; Robert Mills; Bhāgavātula Viswa Nath; Gaston Nilié-Martin; Thomas Peers Parkes, B.Sc.; David Henry Peacock, B.A., B.Sc.; B. Venkata Rao, B.A.; Percy James Raymond; Joseph Reilly, B.A.; John Fraid Richardson; Noël Douglas Ridsdale; William Bristow Saville; Lionel Gowing-Scopes; Bernard Charlie Smith; John Henry Smith; George Alfred Stokes; Kapibram Hardevram Vakil, B.A.; Ernest Vanstone, B.Sc.; Alexey Mikhailovich Vassiliev; Harry James Vipond, B.A.; George Wishard, B.A.; Ernest Walter Wright.

Of the following papers, those marked * were read:—

*308. "Chemical Examination of the Root of *Ipomoea orizabensis*." By FREDERICK BELDING POWER and HAROLD ROGERSON.

The material employed for this investigation consisted of the root of *Ipomoea orizabensis*, Ledanois (Nat. Ord. *Colvolvulaceae*), commonly known as "Mexican Scammony Root."

The root contained 14.55 per cent of resin, 71 per cent of which was soluble in ether. After purification with animal charcoal, the resin was obtained nearly colourless. It then melted at 125–130°, and had $[\alpha] -23.0^\circ$.

For a complete examination of the root, 48.76 kilograms. of the ground material were extracted with hot alcohol. The resulting extract, when distilled in a current of steam, yielded a small amount of a pale yellow essential oil.

From the portion of the extract which was soluble in water the following compounds were isolated:—(i.) scopoletin, $C_{10}H_8O_4$; (ii.) 3:4-dihydroxycinnamic acid, $C_9H_8O_4$, from which the methyl ester (m. p. 158–160°) was prepared. The aqueous liquid contained, furthermore, a quantity of sugar, which yielded *d*-phenyl-glucosazone (m. p. 205–206°, and from a portion of the original alcoholic extract a small amount of sucrose was also obtained.

The portion of the alcoholic extract which was insoluble in water consisted of a resin which possessed the above-mentioned characters. This resin, by successive extraction with various solvents, was resolved into a number of products which were for the most part amorphous, and not entirely glucosidic, but by the further treatment of these products many well-defined substances were obtained. It has thus been shown that the resin is exceedingly complex in character, and it follows that the so-called "jalapin," which includes all those constituents of the resin which are soluble in ether, cannot be represented by any of the various formulæ hitherto assigned to it.

*309. "The Constitution of Ergothioneine: a Betaine Related to Histidine." By GEORGE BARGER and ARTHUR JAMES EWINS.

Ergothioneine, $C_9H_{15}O_2N_3S$, a crystalline base isolated from ergot by Tanret in 1909, has been found to be a betaine of thiolhistidine (α -amino- β -2-thioglyoxaline-4(or 5)-propionic acid).

On boiling with 50 per cent aqueous potassium hydroxide trimethylamine is eliminated, and an acid, $C_6H_6O_2N_3S$ (β -2-thioglyoxaline-4(or 5)-acrylic acid is obtained. On oxidation with dilute nitric acid the latter yields β -glyoxaline-4(or 5)-acrylic acid, from which on reduction β -glyoxaline-4(or 5)-propionic acid is produced.

The treatment of ergothioneine with ferric chloride leads to the formation of histidine-betaine.

*310. "The Methane Equilibrium." By JOHN NORMAN PRING and DORIAN MACEFIELD FAIRLIE.

Carbon was heated electrically in hydrogen at definite known temperatures between 1100° and 2000°, and under pressures between 10 and 200 atmospheres. The velocity of the formation of methane was found to increase rapidly with the pressure, and to proceed to a final equilibrium stage.

As would follow from the law of mass action for a true equilibrium, the value of $p\text{-CH}_4/p\text{-(H}_2\text{)}^2$ was always found to be constant under different pressures if the temperature were the same, and the same modification of carbon used.

With amorphous carbon, temporary equilibrium values were obtained, in which at all temperatures the amount of methane was greater than that corresponding with the true equilibrium with graphite. The relative difference between the equilibrium values for amorphous carbon and graphite increases with the temperature. It follows from this, by applying Kirchhoff's law, that the mean specific heat of amorphous carbon is, at all the temperatures concerned in this work, higher than that of graphite, and that the difference increases with the temperature.

No appreciable effect was exerted by high pressures on the yield of acetylene and ethylene, and no other hydrocarbon was formed.

*311. "The Decomposition of Nitric Acid by Light." By WILLIAM COLEBROOK REYNOLDS and WILLIAM HENRY TAYLOR.

The authors have investigated the decomposition of nitric acid by light, and find that the reaction is reversible, the products of decomposition slowly re-combining more or less completely in the absence of light. The extent of the decomposition and re-combination was illustrated by a series of curves. They have proved that pure anhydrous

nitric acid decomposes very slowly in the dark, giving the same products of decomposition.

DISCUSSION.

Dr. VELEY expressed his satisfaction that the authors had amply confirmed the conclusion drawn from certain elementary experiments by Manley and himself (*Phil. Trans.*, 1908, A, xcxi., 367) that the vapour of nitric acid rather than the liquid is decomposed by sunlight. The observations of the authors that the reaction $4\text{HNO}_3 = 2\text{H}_2\text{O} + 2\text{N}_2\text{O}_4 + \text{O}_2$, is reversible on alteration of conditions, appeared to be of especial interest, and was in accordance with results obtained in the study of other reactions in which nitric acid took part.

More information might possibly have been obtained from the authors' results if sunshine records had been given; although it was shown that the actinic effect of the sun was greater in August than in May, a result to be expected, yet the difference found between the effects in May and March was almost inappreciable, a result contrary to general experience.

Prof. T. TURNER asked for information as to the method whereby the pressure in the tubes had been estimated, and how the gases were collected and measured. It was also suggested that by means of a capillary tube closed at the upper end and inserted inside the closed tube, a continuous series of pressure observations might perhaps be taken, instead of only determining the final pressure at the end of the test.

Dr. SCOTT asked whether the authors had considered the possibility of traces, especially of hydrochloric acid and of iron, acting as catalysts. These and other substances which might act thus might conceivably come from the glass apparatus used.

The curves of the pressures obtained with the various proportions of liquid and vapour space were remarkable in the case of a reversible action.

Mr. REYNOLDS, in reply to Dr. Scott, stated that it was possible that traces of iron and chlorine too small to be detected by the ordinary reagents were present in the acid employed through contact with glass. If such traces affected the results, it was, however, curious that the phenomena were so regular when different samples were employed, and that in clear silica tubes rather greater decomposition occurred than in glass; moreover, as only the vapour was decomposed, it was unlikely that iron affected the phenomena.

*312. "Derivatives of *o*-Xylene. Part I. 3-Nitro-*o*-xylene and 3:6-Dinitro-*o*-xylene." By ARTHUR WILLIAM CROSSLEY and GERTRUDE HOLLAND WREN.

3-Nitro-*o*-xylene has been prepared from 3:4-dinitro-*o*-xylene by reduction with stannous chloride to 3-nitro-*o*-4-xylidine, and replacement of the amino-group in this substance by a hydrogen atom. A comparison of the properties of 3-nitro-*o*-xylene obtained in this way with the 3-nitro-*o*-xylene isolated from the products of the action of a mixture of nitric and sulphuric acids on *o*-xylene (*Trans.*, 1909, xciv., 208) shows that the latter contains some of the isomeric 4-nitro-*o*-xylene, probably about 7 per cent.

3:6-Dinitro-*o*-xylene (compare *Trans.*, 1909, xciv., 210) has now been obtained in a pure condition from the products of direct nitration of *o*-xylene. It crystallises from alcohol in sheaves of needles, melting at 89–90°.

*313. "Derivatives of *o*-Xylene. Part II. Dinitro-*o*-xylidines." By ARTHUR WILLIAM CROSSLEY and GEORGE FRANCIS MORRELL.

Attempts to prepare 3:6-dinitro-*o*-xylene by conversion of 3:4:6-trinitro-*o*-xylene into 3:6-dinitro-*o*-4-xylidine and elimination of the amino-group from this substance have been unsuccessful. The nitro-group in position 3 is the one attacked by reducing agents.

In the course of the experiments five of the six theoretically possible dinitro-*o*-xylidines have been prepared, and their properties were described. The missing 3:6, dinitro-*o*-4-xylidine (I.) is the one which it was desired prepare for the initial object of this research.

FARADAY SOCIETY.

Ordinary Meeting, December 6th, 1911.

Dr. J. A. HARKER, F.R.S., in the Chair.

DR. F. J. BRISLEE presented a paper, entitled "*A Redetermination of the Density and Coefficient of Lineal Expansion of Aluminium.*" (Will be inserted in full).

DR. V. H. VELEY, F.R.S., read a paper on "*The Solution Volumes of Nitric Acid*" (see p 309).

A paper by Dr. J. N. PRING and Mr. J. R. CURZON, B.Sc., on "*The Influence of the Physical Condition of Metals on Cathodic Overvoltage,*" was read by Dr. Pring.

The overvoltage during the liberation of hydrogen on a metallic cathode was found to be dependent to a considerable degree on the condition of the metal. Comparatively large differences were usually obtained with the same metal when in the different physical conditions produced by annealing, hardening, and electro-depositing. In the case of copper the maximum overvoltage is given with the hard metal, while in the case of iron the reverse is the case, the lowest overvoltage accompanying the hardest condition.

Metals which have been deposited electrolytically, in some cases, as with copper, give the maximum values for those metals; and in other cases, as with nickel and iron, give minimum values.

The current density at which a metal is deposited has also usually a small effect on the overvoltage.

The CHAIRMAN said that it was sometimes necessary to test long lengths of alloy wire, such as platinum-iridium, for homogeneity, and he suggested that some such method as the author's might be applied in this connection.

DR. F. M. PERKIN pointed out that electro-deposited metals, such as iron, often contained impurities depending on the dilutions used, and these would affect the measurements obtained.

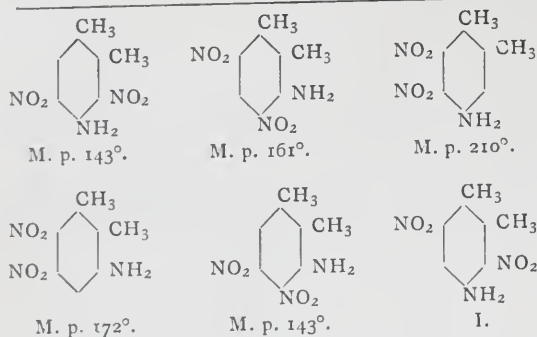
DR. J. N. PRING saw difficulties in Dr. Harker's suggestion, as the overvoltage increased with time and small effects might be obscured.

MR. W. R. COOPER exhibited and described some of the latest forms of the Benkoe Primary Battery.

The elements of this cell are carbon and zinc, and the electrolyte a bichromate solution, preferably of the sodium salt. Its essential feature is the use of a porous carbon electrode through which the electrolyte flows under pressure, thus reducing polarisation to a minimum. The carbon, which is the external element, is shaped like a flattened cylinder and is covered with a shell of lead. In the small space between the two the electrolyte is introduced under a head and it flows right through the carbon to the zinc and thence to waste.

The e.m.f. is 2 volts, and a cell weighing 10 lbs. (excluding electrolyte), and having dimension $9\frac{1}{4}$ ins. high, $6\frac{1}{4}$ ins. long, and $1\frac{1}{4}$ ins. wide, gives a steady current up to, say, 25 ampères at 1.5 volts. The normal flow of electrolyte is $\frac{1}{2}$ litre per hour per cell, and the internal resistance is below 0.01 ohm, which is very low. Since there is no difficulty in keeping it in order, the cell is very suitable for laboratory work, or where the cost of running is not of prime importance.

In a new form of cell exhibited the electrolyte passes through the carbon by diffusion, very concentrated electrolyte being introduced into the outer and water into the inner compartment; or fairly strong sulphuric acid may be used in the outer and strong bichromate solution in the inner compartment. In either case the solution round the zinc is very slightly acid and a zinc efficiency of 90 per cent is claimed. Obviously the diffusion type cannot give current continuously like the pressure type, but the cells are likely to prove very useful in telegraphy, motor-car lighting, and for hand-lamps. Probably, too, a successful miners' lamp will be produced, capable of burning for two periods of eight hours on consecutive days. This has



DISCUSSION.

DR. MORGAN drew attention to the interesting analogy existing between the interaction of alcoholic ammonia and 3:4:5-trinitro-*o*-xylene and 3:4:6-trinitro-*o*-xylene, whereby the mobile nitro-groups (4-NO₂ and 3-NO₂ respectively) were replaced by amino-groups, and the formation of aromatic amines from 1-chloro-2:4-dinitrobenzene or 1:2:4-trinitrobenzene, in which a mobile chloro- or nitro-radicle is directly replaced by an amino-group. This extreme mobility of the chloro- or nitro-radicle was conditioned by the presence of two other nitro-groups in ortho-para- or di-ortho-positions with respect to the reactive substituent (compare Hepp, *Annalen*, 1882, ccxv., 363).

314. "*The Absorption of the Halogens by Dry Slaked Lime.*" By WILLIAM ARTHUR REGINALD WILKS.

It was shown that bromine is absorbed from carbon tetrachloride solution by slaked lime (dried in a vacuum), with the production of an "adsorption compound," which is brick-red. The colour of "bromine bleaching powder" is due to this product. Iodine gives a similar adsorption compound, which is almost black.

The concentrations of bromine in the solution (C₂) and in the lime (C₁) are connected by the formula—

$$\frac{C_1}{C_2^n} = k,$$

when *n* is one-third. The adsorption of iodine obeys a similar formula, *n* being still one-third, but the constant *k* has a value different from that of bromine.

Adsorption phenomena could not be detected when chlorine was absorbed by dry slaked lime under the same conditions as before, but the results showed that in this case a chemical compound was formed.

315. "*A Method of Determining Carbon and Nitrogen in Organic Compounds.*" By EDWARD PERCY FRANKLAND.

With reference to the author's method for the simultaneous determination of carbon and nitrogen in organic substances (*Trans.*, 1911, xcix., 1783), his attention has been drawn to the fact that similar determinations were made by Klingemann (*Annalen*, 1893, cclxxv., 92), using a gas apparatus for the estimation of nitrogen and carbon dioxide. Whilst aware that Dr. Klingemann had carried out an investigation on the production of nitric oxide during the combustion of nitrogenous substances in a vacuum (*Ber.*, 1889, xxii., 3064), the author regrets that he was not previously cognisant of the fact that determinations of carbon in organic compounds had been made by the Frankland-Armstrong process, and that, therefore, he was unable to make reference to Dr. Klingemann's second communication on this subject.

The author considers that the principal advantage of the process as described by him lies in the avoidance of all complicated apparatus for gas analysis, thus rendering the method of more general utility.

(To be continued.)

already been accomplished on the laboratory scale, but it remains for such lamps to be put into actual use.

The meeting concluded with a description by Dr. T. M. LOWRY of several types of thermostats and devices used therewith, exhibited by Mr. Bousfield, Dr. Cumming, Dr. Lowry, Prof. Marshall, and Dr. A. Slater. Dr. Lowry also exhibited some silica mercury lamps suitable for spectroscopic and polarimetric work.

The following papers were presented:—

"Notes on Thermostats," by Prof. HUGH MARSHALL, D.Sc., F.R.S. (see p. 295).

"Notes on Two Thermo-regulators," by Mr. W. R. BOUSFIELD, M.A., K.C. (Will be inserted in full).

"Notes on Thermostats and Devices used in connection with Thermostats," by Dr. A. C. CUMMING (see p. 307).

Prof. F. G. BAILEY, in a communication read to the meeting, supplemented the descriptions given in the papers of regulators used in conjunction with electric heating by an account of Dr. J. Gibson's regulator. The electrical relay is operated by the town supply and is joined in series with a high resistance. The mercury-contact short-circuits the relay coils instead of breaking the current, so sparking is reduced to a minimum. He further dwelt on the importance of very vigorous stirring in connection with electrical heating.

Mr. E. P. HOLLIS referred to the difficulty experienced by a firm of explosive makers in attempting to devise an electrical arrangement for maintaining the temperature of a large room constant to 1° C.

Mr. E. H. RAYNER said that at Potsdam a similar problem had been solved by heating the room under a false floor of open bricks.

NOTICES OF BOOKS.

Experiments for Engineering Students in General Chemistry. By JOSEPH H. JAMES, B.Sc., Ph.D., and JOHN A. SCHAEFFER, A.M., Ph.D. New York: McGraw Hill Book Co. 1911.

THIS book is a manual of experimental chemistry, specially adapted for the use of engineering students who are taking a general scientific course before embarking upon their technical studies. It was written for the students of the Carnegie Technical Schools, and embodies the author's views as to the laboratory work which should be done in order to stimulate the interest of the engineering student and simultaneously give him an insight into the main principles of chemistry. It differs but slightly from an average general laboratory guide, and cannot be said to offer any special advantages or novelty of treatment. Much space is wasted in giving minute details for the performance of very simple manipulations, such as a demonstrator could show the student in a very short time in the laboratory, and the directions are frequently unnecessarily full for any but very young students.

Grundzüge der Dispersoidchemie. ("Outlines of Dispersoid-chemistry"). By Prof. Dr. P. P. von WEIMARN. Dresden: Theodor Steinkopff. 1911. (4 Mk.).

THIS book has been translated from a Russian manuscript which was based upon a lecture delivered at St. Petersburg by the author in 1910. The work of translation has necessarily delayed the appearance of the German text, and the author, unwilling to cause further delay, has unfortunately been unable to discuss fully the results of his latest work in confirmation of his dispersoid theory, although some tables of results are given. The book will be read not so much for a critical examination of the whole field covered by the theory as for the strongest possible statement of the author's case—and for this it can be recommended. He shows himself a clear thinker and a lucid

expositor, and it is quite evident that he by no means regards the question as settled, for he strongly urges the need for much carefully planned and systematically carried out work.

Einführung in die Kolloidchemie. ("Introduction to Colloidal Chemistry"). By Prof. D. VIKTOR PÖSCHL. Third Edition. Dresden: Theodor Steinkopff. 1911. (2 m.).

No other branch of natural science has grown in recent years with such extraordinary rapidity as colloidal chemistry, and a monograph on the subject is no sooner published than, in some details at any rate, it is behind the times. Moreover, the science in the last few years has shown unexpected developments of great importance, and the author has had no easy task in revising the book, although the present is the third edition which has appeared since 1908. However, he has shown good judgment and wide knowledge in selecting his new material and carrying out the necessary revision. Methods of preparing colloids are fully treated, and the use of the ultramicroscope is explained. Recent views on the nature of the colloidal condition are treated in detail, as well as the importance of colloidal chemistry in other sciences and in chemical industry and technics. The monograph is replete with references to the most recent literature and the newest books, and provides an excellent survey of colloidal chemistry in a very succinct form.

CORRESPONDENCE.

THE CHANCES OF THE ENGLISH CHEMIST.

To the Editor of the Chemical News.

SIR,—In his letter on the chances of the English chemist, your correspondent of December 15th (CHEMICAL NEWS, civ., p. 292) draws attention to a condition of things which is only now beginning to be generally recognised, and which is operating most disastrously both for the English chemist and the future of British industry. May I, for the information of your correspondent and others who may be interested in the welfare of the English chemist, call attention here to the Association of Chemical Technologists, which was founded on March 29th, 1911. The direct purpose of the Association is to effect a radical change in the very unsatisfactory state of affairs which exists in connection with the application of chemistry to the arts and manufacturing industries in Great Britain. The objects of the Association are:—

1. To extend the study and practice of applied chemistry so as to enable this country to compete industrially on equal terms with the most favoured and commercially progressive countries abroad.
2. To broaden the field of operations for applied chemistry, and for the employment of applied chemists in Great Britain.
3. To place the profession of applied chemistry upon such a sound and proper basis that the applied chemist may be at no disadvantage in comparison with his fellows in allied professions.
4. To promote a wider general appreciation of the value to the country of applied chemistry, and to obtain for it from scientific men, and from the public, the active support and encouragement which, from its great economic importance, it deserves.
5. To encourage and to aid chemists to adopt applied chemistry as a profession, and thereby to promote their interests.
6. To effect the co-operation of applied chemists for all matters which may directly or indirectly promote their interests.
7. To raise a fund to furnish grants for assisting persons approved by the Council to obtain training in

applied chemistry at approved institutions or chemical works, either in this country or abroad, and to furnish grants for the prosecution of technical research.

8. To maintain a register of members of the Association who are seeking technical appointments, and to inform them of suitable applications for their services.

9. To form distinct sections of the Association, each section to have its President, Honorary Secretary, and Council, with the object of enabling technical chemists to keep in touch with one another.

The Association concerns itself broadly and specifically with technical chemists. Although the Association has been in existence only a few months the membership is already large and representative, and includes the names of English chemists from all parts of the world. The enthusiasm of the members is proof of the need of the Association. Your correspondent has asked how the present condition of things may be remedied; the answer is that the remedy must be sought in appreciation of the fact that the future commercial prosperity of the country depends essentially on the scientific application of chemistry in the industries, and consequently on the work of the technical chemist.—I am, &c.,

J. WILBERFORCE GREEN.

30, Victoria Street, Westminster, S.W.

THE CHANCES OF THE ENGLISH CHEMIST.

To the Editor of the Chemical News.

SIR,—I beg you will allow me to endorse the views of your correspondent, Mr. J. S. Morrison, in the *CHEMICAL NEWS* (vol. civ., p. 292).

The English chemist, and especially the "routine" chemist, so often maligned by the research enthusiasts, and yet capable of work extremely valuable to his firm, is not generally treated in such a manner as to lead him to take an interest in his work, thus rendering it attractive to him.

I submit that a man who has experienced a scientific education, with its necessary application to study and its heavy expense, should at least be able to look forward to a reasonable and regular advancement in salary, and thus be placed on the level of the bank clerk and civil servant. Such increase in salary has an influence on the chemist far beyond its value in pounds, shillings, and pence.

The knowledge that a man's employers regard him as something superior to a machine that has to turn out the maximum of work for the absolute minimum of expenditure, gives that man more self-respect, and raises him to a higher plane, and the knowledge that consistently good and faithful work and length of service will not be unrecognised tends in the same direction.

Your correspondent speaks of tar-works, and as a chemist in a large and important tar-distillery, I can personally testify to the fact that great saving can be effected by conscientious laboratory routine work in that industry.

It would benefit both the firm and its chemical staff if the latter were awarded an annual bonus dependent on the profits of the undertaking, and the interest of chemists and manufacturer would be securely welded if this annual bonus were invested in the firm's capital.

Manufacturers should realise that work done in a cheerful and willing manner is likely to be much more beneficial to them than that accomplished by one who, through miserable remuneration and wretched prospects, has the spirit crushed out of him.

The men who will give best service, other things being equal, are those who, largely owing to the attitude of their employer,—

"Carry music in their heart
Through dusky lane and wrangling mart."

—I am, &c.,

HUGH W. JAMES, A.R.C.S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 21, November 20, 1911.

Action of Hydrogen Peroxide on Oxygen Compounds of Iodine.—V. Auger. — Neutral alkaline periodates are reduced to iodates by the action of hydrogen peroxide. Basic sodium periodate is very slowly decomposed by H_2O_2 and transformed into iodate. When 3 per cent H_2O_2 is added to a solution of HIO_4 containing 2 grms. per litre, reduction instantly occurs and oxygen is evolved. A slight brown coloration is produced by the trace of iodine liberated. If a concentrated solution of the acid is used and a large excess of hydrogen peroxide, a considerable amount of iodine is liberated. Oxygen is slowly disengaged from a saturated solution of sodium iodate to which 3 per cent H_2O_2 is added. Solutions of H_2O_2 slowly decompose iodic acid, iodine being deposited; if the solution contains more than 0.8 per cent HIO_3 , the iodine is subsequently oxidised.

Determination of Urea.—MM. Desgrez and Feuille. —The authors describe a method of determining urea which is a modification of Bouchard's method. The urea is decomposed by means of Millon's reagent in a special apparatus, the temperature being raised to 30–35°, and the reaction takes about twenty to twenty-five minutes for completion.

Derivatives of Cyclopentanone.—Marcel Godchot and Félix Taboury.—In a previous communication the authors described the preparation of a new ketone, $C_{13}H_{16}O$, by the hydrogenation of cyclopentanone. To this ketone they provisionally ascribed the formula of α -cyclopentylcyclopentanone. This conclusion they have now confirmed as follows:—On reduction the new ketone gives an alcohol $C_{10}H_{18}O$, which is identical with that obtained from Wallach's unsaturated ketone, prepared by the condensation of two molecules of cyclopentanone with elimination of a molecule of water.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlv., No. 15, 1911.

Sulphur and Nitrogen Derivatives of Phthalic Acid.—Arnold Reissert and Hermann Holle. —Thiophthalic acid anhydride can be prepared by dissolving phthalic acid anhydride in sodium sulphide solution and decomposing the disodium salt obtained with acids. When thiophthalic acid anhydride is dissolved in sodium sulphide the disodium salt of dithiophthalic acid is formed. Thiophthalanil can be obtained by dissolving phthalanil in xylol and adding finely powdered phosphorus pentasulphide. The sulphur atom in this compound can easily be replaced by the divalent residue of ammonia or primary amine bases.

Dehydrogenisation by Catalysis.—N. Zelinsky. —The dissociation of hexamethylene and methyl hexamethylene into hydrogen and benzene or toluol is very strongly influenced catalytically by platinum and by palladium. This dehydrogenisation-catalysis begins at 170° and reaches its maximum at 300°. At a low temperature and in an atmosphere of hydrogen palladium induces the reverse reaction—the hydrogenisation of benzene. Palladium is a specific dehydrogenisation catalyst for cyclohexane-hydrocarbons.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 2nd.	} Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "The Childhood of Animals," by P. Chalmers Mitchell, LL.D., D.Sc., F.R.S.
THURSDAY, " 4th.	
SATURDAY, " 6th.	

INDEX.

- A**BEGG, R., F. Auerbach, and R. Luther, "Messungen Elektromotischer Kräfte Galvanischer Ketten mit Wässrigen Elektrolyten" (review), 149
- Aberdeen University, 131
- Aberystwyth, University College of Wales, 124
- Abney, Sir W. de W., colour blindness and the trichromatic theory of colour vision, 238
- Ahoulenc, J., and J. B. Senderens. (See Senderens, J. B.)
- Absorption bands in solution, influence of solvent on position of, 249
- Acetaldehydphenylhydrazones, isomeric, 279
- Acetamide, preparation, 1
- Acetone, electrochemistry of solutions in, 280
- ethyl derivatives, 72
- Acetones, aromatic, action on mono-sodium derivative of benzyl cyanide, 209
- Acetylcellulose, celluloid from, 203
- Acetylene, use in laboratories, 72, 172
- Acheson, E. G., deflocculation, 243
- researches on electric furnace products, 268
- Acid, acetic, purification and properties of, 19
- α -amino *n*-nono, polypeptides of, synthesis, 230
- benzenesulphobenzonic, 198
- α -bromobutyric, action of isobutylamine and diisobutylamine on, 84
- camphoric, synthesis, 280
- cinnamic, and cinnamic acid ester, complex mercury compounds of, 47
- cyclohexanone - 4 - carboxylic, molecular configuration of oxime of, 302
- cyclopentanone - 4 - carboxylic, formation, 288
- damascenic, synthesis, 286
- s - dibromosuccinic, action of benzylamine on, 228
- dithiocamphocarbonic, 197
- formic, catalytic decomposition, 11
- series, catalytic preparation of ether salts of acids of, 84
- galloannic, acid character, 230
- hexahydrohippuric, 36
- hexaridic, action on starch and dextrine, 137
- hydrofluoric, action on zirconium oxide, 161
- isopropionic, action of oxidising agents on, 174
- lactarinic, 294
- obtained from mushrooms, 232
- lactic, action of ultra-violet rays on, 24
- l*-malic, influence of inactive electrolytes on optical activity in aqueous solution, 242
- metaphosphoric, hydration, 221
- hydratisation, 120
- β -2-methoxyphenylpropionic, 277
- 2 - methylamino - 3 - methoxybenzoic, synthesis, 286
- Acid, 1-methylcyclohexylidene-4-acetic, molecular configuration, 302
- optically active derivatives 230
- nitric, action on bornylene, 266
- gallic acid trimethyl ether and pyrogallocarboxylic acid trimethyl ether, 230
- decomposition by light, 315
- solution volumes of, 309
- nitrous, action on bornylene, 266
- paraoxyphenylglyoxylic, 209
- phenolsulphonic, method for determination of nitrates in water, 146, 159, 167, 178
- phosphoric, action of syrupy, on alloys obtained in an electric furnace, 118
- colorimetric determination, 174
- phthalic, sulphur and nitrogen derivatives, 318
- picric, colour and molecular state, 265
- purpuric and oramil, analogues of, 229
- salicylic, Kobert's reaction as test for, 244
- silicic, preparation of colloidal, 161
- $\alpha\alpha$ -tetramethylpimelic, 84
- tricarballic, reactions of imino-compounds leading to formation of, 240
- 3 : 4 : 5-trichloropicric, and derivatives, interactions, 241
- Acids of formic acid series, catalytic preparation of ether salts of, 84
- alkylaminodithiocarbonic, salts and ethers of, 119
- alkylglutaconic, having one mobile hydrogen atom, reactions of, 268
- aromatic, catalytic etherification, 137
- azoic, preparation of ortho-substituted, 174
- benzylalkylacetic, preparation of asymmetric, 173
- β -chlorocinnamic, 239
- cohenillic and carminic, substances related to, 239
- cyclopropanedicarbonic, transformation of substituted paracarbonic acids into isomeric, 174
- diabasic, catalytic etherification, 283
- dithiocarbonalkylamino, salts and acids of, 306
- fatty, latent heat of fusion and specific heat, 185
- preparation of ketones of higher, 287
- with acetylene function, oxidation of higher, 72
- glutaconic, chemistry of, 268
- hydroxybenzoic, oxidation products of, 22
- iridoxalic, new types of, 72
- ketoglutaric, 150
- nitric, action on aloins constitution of nitro derivatives obtained by, 173
- organic, containing alcoholic hydroxyls, basicity of, 258, 282
- separation of mixtures of, by partial esterification, 287
- paracanic, transformation of substituted, into isomeric cyclopropanedicarbonic acids, 174
- Acids, paraoxyphenylaminoacetic and paramethoxyphenylaminoacetic, ureins of, 29
- Aconastics, experiments in, 255
- Acrolein, monobrominated, properties of, 306
- Astinium, atomic weight, 59
- α -particles emitted by active deposits of, 289
- Acylanilides, chlorination, 22
- Adams, L. H., and J. Johnston (See Johnston, J.)
- Adherence of flat surfaces, 276
- Affinity, role in dyeing, 36
- values, use of indicators for determining, 115
- Africa, French West, composition of oil-seeds from, 174
- Agglutination, factors concerned in, 301
- Agulhon, H., colorimetric detection of alcohol in presence of acetone, 257
- Aiazzi-Mancini, M., A. Angeli, and L. Alessandri. (See Angeli, A.)
- Alcohol, absolute, and calcium, hydrogenation by, 137
- colorimetric determination in presence of acetone, 257
- electromotive forces in, 22, 265
- hydrogen electrode in, and influence of water on its electromotive force, 265
- Alcohols, acid, action of thionyl chloride on ethers of, in presence of a tertiary base, 108
- etherification by hydrazides, 24
- α -ketonic, synthesis of tertiary, 11
- photolysis by ultra violet rays, 197
- pinacolic, catalytic dehydration of secondary and tertiary, 253
- Alcoholates, metallic, 306
- researches on, 293
- Alcoholysis of Japan wax, 138
- Aldehyde, crotonic, hydrogenation in presence of nickel, 294
- figure of butter, 305
- reaction, Angeli-Kimini, 253
- tetrollic, 59
- attempts to prepare, 306
- Aldehydes, acid, of succinic series, 150
- action on pyrrol derivatives, 282
- anisic and piperoylic, action on sodium derivative of benzyl cyanide, 186
- Aldehyde hydrazine, 48
- Aldoximes, syn., preparation, 250
- Alessandri, L., and A. Angeli. (See Angeli, A.)
- Alexander, F. W., "Metropolitan Borough of Poplar, Annual Report for 1910" (review), 208
- Alkali fluorides, fluorhydrates of, 72
- sulphates, decomposition of cerium earth double sulphates with, 179
- Alkalis, action on chloraloses, 47
- of chlorine on, 265
- behaviour of copper salts with, 286
- Alkaline condensations of nitro-hydrazo-compounds, 250
- earths, perbromides and periodides of metals of, 210
- electrical properties, 293
- Alkaline metals, fluorescence, 186
- preparation, 59
- Alkali compounds of stannous series, 60
- Alkylammonium series of nitrites, 279, 304
- Alkyl bromides, velocity of addition to cyclic tertiary bases, 302
- iodides, action on copper oxide, 210
- Allium sativum, action on lead and mercury, 251
- Alloys obtained in an electric furnace, action of syrupy phosphoric acid on, 118
- Aloins, constitution of nitro-derivatives of, 258
- obtained by action of nitric acids on, 173
- Ally, J. and V. Brustier, catalysis of borneol and catalytic hydrogenation of camphur, 198
- and C. Rabaut, *p*-oxyphenylglyoxylic acid, 209
- ureins of *p*-oxyphenylaminoacetic and *p*-methoxyphenylaminoacetic acids, 29
- Aluminium hydroxide, precipitation in granular form, 35
- sulphide, 162
- Amides, hypobromous, 245
- hypiodous, 306
- Amines, action on 2-phenyl-1 : 3-benzoxazine-4-one, 20
- and phosphates of uranyl, 47
- Aminoalkylglyoxalines, 286
- Ammonia, action of silent discharge on dry, and on wet, 137
- on chloraloses, 71
- on mercurous nitrate, 210
- on 2-phenyl-1 : 3-benzoxazine-4-one, 20
- and pyridine, separation and determination, 193
- and water compounds, 210
- cuprous, composition of complex, 230
- production by heat, 11
- role of iron as catalyst in synthesis of under pressure, 161
- use of liquid, in chemical reactions, 293
- Ammonium bases, preparation of nitrites of primary, secondary and tertiary, 253
- compounds, asymmetric quaternary, 279
- electrode, 253
- salts, influence of the medium and of light on decomposition of quaternary, 96
- crucialite, 162
- cyanate, transformation into carbamide, 287
- Anderson, B. R., study of the fruit of *Solanum dulcamara*, 2
- André, E., new method of obtaining β -diketones, 59
- Andrews, A. E., active constituents of Indian solanaceous plants, *Datura stramonium*, *D. fastuosa*, and *D. metel*, 266
- E. R., J. H. Coste, and E. T. Shelbourn. (See Coste, J. H.)
- Angeli, A., and L. Alessandri, nitropyrrrol, 11

- Angeli, A., and L. Alessandri, researches on azoxy-compounds, 234
- and M. Aiazzi-Mancini, researches on the N-phenyl ethers of oximes, 48
- Angeli-Rimini aldehyde reaction, 258
- Anhydrides, acid, action on monosodium derivative of benzyl cyanide, 72, 193
- photolysis by ultra-violet rays, 197
- Anilides, chlorination of, 22
- Aniline and benzaldehydecyanohydrin, effect of heat on mixture of, 240
- Animal organisms, origin and destiny of cholesterol in, 301
- Anisallyaldehyde, transformation in various solvents, 285
- Antigene and antibodies, 25, 39, 55
- Antimonic substituents, orienting influence in benzene nucleus, 285
- Antimony and manganese, ferromagnetic compounds, 270
- in all vs. volumetric method for determining, 81
- in copper, determination, 82, 91
- organic derivatives, 285
- hydride, determination of solid, 36
- selenium, metallography of system, 156
- Antipyrine and ferric chloride compounds, 246
- Apparatus for sublimation in a vacuum, 251
- mine rescue, 7
- sulphuretted hydrogen, 189, 256
- Ark, H., and H. M. Dawson. (See Dawson, H. M.)
- Armstrong, H. E., E. F. Armstrong, and E. Horton, herbage studies, 276
- Arnaud, A., and V. Hasenfratz, oxidation of higher fatty acids with acetylene function, 72
- Arndt, K., "Die Bedeutung der Kolloide für die Technik" (review), 306
- Arnold, J. O., and A. A. Read, chemical and mechanical relations of iron, chromium, and carbon, 257
- Aromatic compounds, relation of velocity of chlorination of, to constitution, 22
- Arrhenius, S., applications of physical chemistry to the decline of immunity, antigene and antibodies, 25, 39, 55
- Arsenic, allotropic modifications and melting-point, 118
- and manganese, ferromagnetic compounds, 270
- and tin compounds, 24
- in copper, determination, 82, 91
- pentoxide, hydrates of, 120
- Association of Teachers in Technical Institutions, Annual Meeting, 22
- Astre, Ch., and J. Vidal, compound of antipyrine and ferric chloride, 246
- Atomic theory, development of, 37, 49
- weight of actinium, 59
- of calcium, 184, 190
- of iron, revision of, 48, 64, 79, 88, 113
- of meteoric iron, 48, 113
- weights, annual report of Committee on, 5, 15, 28, 218, 232
- Auerbach, F., R. Aberg, and R. Luther. (See Aberg, R.)
- Auger, V., action of hydrogen peroxide on oxygen compounds of iodine, 318
- Aurates, halogen, of ethylene and propylene diammonium, 48
- Aureli, S., and E. Bargellini. (See Bargellini, E.)
- Australian milk, composition, 305
- Autofermentation of yeast, action of dissolved substances on, 301
- Auxochromes, influence on phototropism, 234
- Auzies, J. A. A., analysis of substance containing C, H, N, O, S, Cl, Br, I, 245
- containing C, H, O, N, 245
- containing C, H, O, N, S, 245
- Azafran, root-dye of, 11
- Azo-compounds, molecular refraction, 293
- Azomethines derived from phenylisoxazolone, 84
- Azoxy-compounds, 234
- BAAR, N., alloys of molybdenum with nickel, of manganese with thallium and of calcium with magnesium, thallium, lead, copper, and silver, 53
- Bachran, F., and A. Stähler. (See Stähler, A.)
- Bahr, F., thallous hydroxide, 120
- Baker, H. B., and A. G. V. Harcourt. (See Harcourt, A. G. V.)
- Balareff, D., hydrates of arsenic pentoxide, 120
- hydratisation of metaphosphoric acid, 120
- rate of hydration of metaphosphoric acid, 221
- Balbiano, L., Angeli-Rimini aldehyde reaction, 258
- Banerjee, M. N., action of Allium sativum or garlic juice on lead and mercury, 251
- Banger, University College of North Wales, 124
- Barbier, P., and R. Locquin, action of organo-magnesium compounds on methyl acetylpyruvate, 198
- new synthesis of methyl ketones, 198
- transformation of substituted paraconic acids into isomeric cyclopropanedicarboxylic acids, 174
- Bargellini, E., and S. Aureli, derivatives of oxyhydroquinone, 234
- G., and E. Martegiani, derivatives of oxyhydroquinone, 198, 234
- Barger, G., adsorption of iodine by glucoside saponarin, 139
- and A. J. Ewins, constitution of ergothioneine, 315
- and W. W. Starling, β -2 methoxy-naphthylpropionic acid and methoxyperinaphthylindrone, 277
- and P. Van Romburgh. (See Van Romburgh, P.)
- Baism, separation and determination in presence of calcium and magnesium, 48
- oxide as a reducing agent, 233
- Barker, S. G., S. W. J. Smith, and W. White. (See Smith, S. W. J.)
- T. V., some new inorganic salts, 23
- Barkla, C. G., and J. Nicol, homogeneous fluorescent X-radiation of a second series, 231
- Barlow, W. E., binary and tertiary alloys of cadmium, bismuth, and lead, 35
- Barratt, T., and E. Marsden. (See Marsden, E.)
- Barrow, F., and A. McKenzie. (See McKenzie, A.)
- Barthe, L., phosphates of uranyl and amines, 47
- Bary, P., and L. Weydert, apparent reversibility of vulcanisation of caoutchouc by sulphur, 245
- Battersea Polytechnic, 135, 150
- Battery, Benkö primary, 316
- Baudisch, O., nitrate and nitrite assimilation, 47
- Bauer, E., and A. Haller. (See Haller, A.)
- Baur, E., hydrothermal silicates, 246
- "Themen der Physikalischen Chemie" (review), 11
- Baxter, G. P., and T. Thorvaldson, atomic weight of meteoric iron, 48
- revision of atomic weight of iron, 113
- and V. Cobb, revision of atomic weight of iron, 48, 64, 79, 88
- Beadle, C., and H. P. Stevens, method for determining amount of insoluble particles in raw rubber, 305
- Beane, Calabar, chemical examination, 285
- Beard, J., "Enzyme Treatment of Cancer" (review), 222
- Bearder E. A., and A. G. Green. (See Green, A. G.)
- Beckman, J. W., electrolytic furnace method for producing metals, 45
- Bequerel, J., propagation of light in fluorescent substances, 305
- Beer, solubility of carbon dioxide in, 20
- Béhal, A., and A. Detouff, new derivative of urea, chlorourea, 245
- Belfast Municipal Technical Institute, 136
- Queen's University, 133
- Beodikt and Weselsky. (See Weselsky)
- Benkö primary battery, 316
- Benner, R. C., fractionation of yttrium earths by means of succinates, 203
- Benzaldehydecyanohydrin and aniline, effect of heat on a mixture of, 240
- Benzaldehydephenylhydrazones, preparation, 287
- Benzene, absorption spectra of chlorine and bromine derivatives of, 240
- of iodine derivatives of, 287
- nucleus, orienting influence of antimonic substituents, 285
- Benzylamine, action on *s*-tribromosuccinic acid, 228
- Benzylamines, preparing, 174
- Benzyl cyanide, action of acid chlorides, acid anhydrides, and ketones on monosodium derivative of, 72
- of anisic and piperonylic aldehydes on sodium derivative of, 186
- of aromatic acetones on monosodium derivative of, 209
- Benzylcyclohexanone, ketones of type of, 150
- Berberin, synthesis, 197
- Berg, A., chromotellurates, 72
- Bergner, E., and A. Sieverts. (See Sieverts, A.)
- Bernardini, L., and G. Calcagni. (See Calcagni, G.)
- Berry, A. J., distillation of binary mixtures of metals in metals in vacuo, 276
- Berthelot, D., and H. Gaudechon, photolysis of alcohols, acid anhydrides, ether oxides, and ether salts by ultra-violet rays, 197
- Beryllium. (See Glucium.)
- Besson, A., action of silent discharge on dry and on wet ammonia, 137
- formation of hydrogen peroxide by electric discharge, 293
- Betaine of tryptophan, preparation and identity with alkaloid hypaphorine, 277
- Bevan, P. V., absorption and dispersion in metallic vapours, 116
- Beyer, J., and S. Hilpert. (See Hilpert, S.)
- Bhattachangy, H. J., use of acetylene in laboratories, 172
- Bigden, A., tetra-alkyl silicates, 233
- Bitz, W., and F. Caspari, aluminium sulphide, 162
- and E. Marcus, ammonium caralite, 162
- Binary system CuBr-KBr, 120
- systems, CuCl-AgCl, CuCl-NaCl, CuCl-KCl, 48
- Binary system of MgCl₂ and CaCl₂ with chlorides of K, Na, Hg, Pb, Cu, Zn, Sn, and Cd, 246
- Bingham, E. C., and G. F. White, "Laboratory Manual of Inorganic Chemistry" (review), 24
- Birds, iridescent colours of, 239
- Birkbeck College, 135
- Birmingham University, 126
- Bisilicates, fusion experiments with, 48
- Bismuth and manganese, ferromagnetic compounds, 270
- cadmium and lead alloys, binary and tertiary, 35
- salts, action of hydrogen and sodium peroxides on, 36
- Blackburn Municipal Technical School, 136
- Blackie, A., behaviour of fused silica at high temperatures, 77, 86
- Blackman, P., funnel support, 30, 211
- height-adjustable burner, 259
- improved funnel, 30, 211, 312
- movable gas distributor, 247
- Blaise, E. B., ketoglutaric acid and acid-aldehydes of succinic series, 151
- and H. Gault, acyclic ketodiacids, 157
- Blanc, G. L., and J. F. Thorpe, Komppa's synthesis of camphoric acid, 280
- Bleaching powder, action of carbon dioxide on, 265
- Block, J. R., and J. G. Parker. (See Parker, J. G.)
- Blount, B., cement, 220, 290
- Blücher, H., "Modern Industrial Chemistry" (review), 149
- Blumenthal, H., and A. Stock. (See Stock, A.)
- P. L., and P. E. Browning. (See Browning, P. E.)
- Bodenstein, M., methods of maintaining constant high temperatures, 9
- Bodroux, F., action of acid chlorides, acid anhydrides, and ketones on monosodium derivative of benzyl cyanide, 72
- and anhydrides on monosodium benzyl cyanide, 198
- of anisic and piperonylic aldehydes on sodium derivative of benzyl cyanide, 186
- of aromatic acetones on monosodium derivative of benzyl cyanide, 209
- of ether salts on monosodium benzyl cyanide, 174
- and F. Taboury, action of bromine in presence of aluminium bromide on cyclohexanol and cyclohexanone, 156
- bromination of cyclohexane, 137
- of hydroaromatic compounds in presence of aluminium bromide, 137
- Boiling-points of metals, 31, 42
- Boismenu, E., hypobromous amides, 245
- hypoiodous amides, 306
- Bonnerot, S., and G. Charpy. (See Charpy, G.)
- Books, Reviews and Notices of—"Acid, Sulphuric, and Alkali, Manufacture of," 10
- "Acidoglobulin, Behaviour of Globulin towards Acids," 71
- "Albuminous Substances, Chemistry of," 185
- "Alkali and Sulphuric Acid, Manufacture of," 10
- "Allen's Commercial Organic Analysis," 174
- "Analysis, Chemical, Technical Methods of," 292
- "Analysis, Organic, Allen's Commercial," 174

- Books, Reviews and Notices of—
 "Analysis, Organic, Handbook of, Qualitative and Quantitative," 256
 "Analysis, Organic, Practical Handbook of," 71
 "Analysis, Qualitative, Systematic," 24
 "Analysis, Volumetric, Systematic Handbook of," 71
 "Anode Rays, Spectra of," 71
 "Apparatus, Spectral, Use of Cylindrical Lenses in," 71
 "Atoms of Carbon, Hydrogen, and Oxygen, Relative Volumes, when in Combination," 161
 "Batteries, Galvanic, Measurements of Electromotive Forces of, with Aqueous Electrolytes," 149
 "Bible, British Museum, Natural History, Guide to Exhibition of Animals, Plants, and Minerals mentioned in," 244
 "Bleaching and Finishing of Cotton, Principles of," 184
 "Bread-making, Technology of," 148
 "British Journal Photographic Almanac, 1912," 305
 "British Museum, Natural History, Guide to Exhibition of Animals, Plants, and Minerals mentioned in the Bible," 244
 "Calculator, Continental Price," 24
 "Cancer, Enzyme Treatment of," 222
 "Cape Province, Notes on the Fertilisers, Farm Foods, Seeds, and Pest Remedies Act," 35
 "Catalysis," 118
 "Cells, Galvanic, Electro-chemical Converters," 185
 "Cellulose, Chemistry of," 10
 "Chemical Theory, Elementary," 24
 "Chemistry, Colloidal, Introduction to," 317
 "Chemistry, Contemporary," 184
 "Chemistry, Dispersoid, Outlines of," 317
 "Chemistry, Elementary Text-book," 231
 "Chemistry, Experiments for Engineering Students in General," 317
 "Chemistry for Beginners," 71
 "Chemistry, Historical, Essays in," 145
 "Chemistry, Inorganic," 10
 "Chemistry, Inorganic, Laboratory Manual of," 24
 "Chemistry, Introduction to," 35
 "Chemistry, Modern Industrial," 149
 "Chemistry of Coal-tar Dyes," 208
 "Chemistry, Organic, for the Laboratory," 24
 "Chemistry, Physical, Essays on," 11
 "Chemistry, Practical, for Medical Students," 221
 "Chemistry, Subject List of Works on, in Library of Patent Office," 281
 "Chemistry, Theoretical, from the Standpoint of Avogadro's Rule and Thermodynamics," 196
 "Chemistry, Treatise on," 231
 "Chemistry, Triumphs and Wonders of Modern," 58, 137
 "Chemists, Famous," 256
 "Cold Storage and Ventilation on Board Ship," 161
 "Colloids in Technology, Importance of," 306
 "Continental Price Calculator," 24
 "Converters, Electrochemical, Galvanic Cells," 185
- Books, Reviews and Notices of—
 "Corrosion of Iron and Steel," 184
 "Cotton, Principles of Bleaching and Finishing of," 184
 "Crystals," 10
 "Crystals, New World of Liquid," 149
 "Decay Processes in Nature," 306
 "Doppler Spectrum of Hydrogen Canal Rays," 71
 "Drugs, Chemistry of Synthetic," 71
 "Dyes, Coal-tar, Chemistry of," 208
 "Dyes, Organic, Investigation and Detection Spectroscopically," 149
 "Egypt, Ministry of Finance, Report on Work of Laboratories in 1910," 209
 "Electrical Nature of Matter and Radio-activity," 232
 "Elements, Lines in Arc Spectra of," 244
 "Enzyme Treatment of Cancer," 222
 "Enzymes, General Chemistry of," 118
 "Equation of Condition," 185
 "Experiments for Engineering Students in General Chemistry," 317
 "Fertilisers, Farm Foods, Seeds, and Pest Remedies Act (Cape Province), Notes on," 35
 "Food, Principal Starches Used as," 184
 "Globulin, Behaviour towards Acids, Acidoglobulin," 71
 "Helium, Researches on," 209
 "Hydrogen Canal Rays, Doppler Spectrum of," 71
 "Indian Association for the Cultivation of Science, Report for Year 1909," 137
 "Iron and Steel, Corrosion of," 184
 "Lenses, Cylindrical, Use in Spectral Apparatus," 71
 "Mathematics, Higher, for Chemical Students," 95
 "Mathematics, Text-book of," 35
 "Matriculation Directory," 221
 "Matter, Electrical Nature of, and Radio-activity," 232
 "Metallurgy of Tungsten," 292
 "Microchemistry, Text-book of," 95
 "Microscope, Cytostallisation, and Discoveries made with it," 232
 "Mineral Substances, Treatise on Analyses of," 58
 "Nature, Decay Processes in," 306
 "Nitrocellulose Industry," 148
 "Œdema," 149
 "Organic Compounds, Identification of," 244
 "Patent Office, Subject List of Works on Chemical Technology in Library of," 281
 "Patent Office, Subject List of Works on Chemistry in Library of," 281
 "Phase Rule and its Applications," 58
 "Photography, Advance of, its History and Modern Applications," 305
 "Physical and Chemical Constants and some Mathematical Functions," 281
 "Physico-chemical Tables," 10
 "Poplar, Metropolitan Borough of, Annual Report for 1910," 208
 "Price Calculator, Continental," 24
 "Radio-activity, Electrical Nature of Matter and," 232
 "Republics, The Ten," 244
 "Soil Solution," 196
 "Spectra, Arc, of Elements, Lines in," 244
- Books, Reviews and Notices of—
 "Spectra of Anode Rays," 71
 "Starches Used as Food, Principal," 184
 "Technology, Chemical, Subject List of Works on, in Library of Patent Office," 281
 "Technology, Importance of Colloids in," 306
 "Tungsten, Metallurgy of," 292
 "Turin Exhibition, 1911, Catalogue of Exhibits of British Chemical Industries Section," 292
 "Ventilation and Cold Storage on Board Ship," 161
 "Winter Specialties," 244
- Boon, A. A., and F. J. Wilson, elimination of bromine from phenyl paramethoxystyryl ketone dibromide, 23
 Borates, tungstic acid, and metatungstates, constitution, 48
 Borned, catalysis, 198
 Bornylene, action of chromyl chloride, nitrous acid, and nitric acid on, 266
 Boron, properties and preparation of the element, 157
 Borough Polytechnic Institute, 135
 Bougault, J., and C. Chavaux, lactic acid, 294
 obtained from mushrooms, 232
 Bourbon, A., and E. Vigouroux, (See Vigouroux, E.)
 Bourgeois, E., and A. Fouassin, formation of aromatic disulphides of type R.S.R'.S.R', and R.S.R'.S.R', 294
 and P. Huber, action of bromonitrobenzenes on thiophenes, 294
 Bourion, F., and G. Darzens. (See Darzens, G.)
 Bourquelot, E., and A. Fichtenholz, glucoside in leaves of pear trees, 197
 Bousfield, W. R., and T. M. Lowry, purification and properties of acetic acid, 19
 Boutaric, A., cryoscopic in fused sodium hyposulphite, 293
 Bowser, L. T., estimation of very small amounts of calcium by means of potassium permanganate, 171
 Boyd, R., and G. G. Henderson. (See Henderson, G. G.)
 Boynton, C. N., and F. A. Gooch. (See Gooch, F. A.)
 Bradford, City of, Technical College, 126
 Bragg, W. H., energy of the X-ray, 291
 radio-activity as a kinetic theory of a fourth state of matter, 110
 Breteau, P., complete destruction of organic matter, 138
 hydrogenation by calcium and absolute alcohol, 137
 by means of nickel and sodium hypophosphite, 119
 by precipitated palladium and sodium hypophosphite, 119
 in presence of divided palladium, 196, 209
 Brinton, P. H. M. F., determination of manganese by the sodium bismuthate method, 94
 Brisbane tidal records, 1908, analysis, 276
 Bristol, Merchant Venturers' Technical College, 126
 University, 125
 British Association, 120
 President's Address, 97
 report of corrosion committee, 164
 Chemical Section, President's Address, 104
 Bromide ferrous, analysis, 64, 79, 88
- Bromination of cyclohexene, 137
 of hydroaromatic compounds in presence of aluminium bromide, 137
 Bromine, action on cyclohexanol and cyclohexanone in presence of aluminium bromide, 136
 and iodine, extraction by chloroform and carbon disulphide, 119
 chlorine and iodine, determination of ratio between, 212, 225
 derivatives of benzene and toluene, absorption spectra, 210
 elimination from phenyl paramethoxystyryl ketone dibromide, 23
 reaction, new characteristic, 119
 Bromonitrobenzenes, action on thiophenes, 294
 Brojewski and Hackwill, M.M., electrical properties of alkaline metals, rhodium and iridium, 293
 Brown, G. E., "British Journal Photographic Almanac, 1912" (review), 305
 J. A., estimation of small quantities of essential oil in spices, &c., 304
 Browne, J. H. B., water supply, 205, 215
 Browning, P. E., modified procedure for detection of silicates, fluorides, and fluosilicates, 296
 and P. L. Blumenthal, decomposition of cerium earth double sulphates with alkali sulphates by fusion with charcoal, 179
 qualitative detection of certain elements which form insoluble sulphates, 284
 Brucine and strychnine, resins, 234
 Bruni, G., and D. Meneghini, formation of metallic solid solutions by diffusion in solid state, 120
 of solid solutions of metals in solid state, 186
 Brustier, V., and J. Aloy. (See Aloy, J.)
 Bryant, E. G., curious thermal phenomenon, 95, 118
 purifying mercury in the laboratory, 149
 Buchner funnel, addition to, 20
 Buckmaster, G. A., and J. A. Gardner, ventilation of lungs in chloroform narcosis, 264
 Budgett, H. M., adherence of flat surfaces, 276
 Bulla, A., and W. Herz. (See Herz, W.)
 Burgess, G. K., melting-points of chemical elements, 165
 and C. W. Waidner. (See Waidner, C. W.)
 M. J., and R. V. Wheeler, lower limit of inflammation of mixtures of paraffin hydrocarbons with air, 279
 Burner, height-adjustable, 259
 Butter, aldehyde figure of, 305
 determination of moisture in, 261
 Butylammonium nitrite and decomposition by heat, 304
- CADMIUM and silver compounds, 209
 bismuth and lead, binary and tertiary alloys 55
 Cæsium fluoride, hydrates of, 11
 Caille, E., preparation of α -naphthalenic ketones by Friedel and Crafts' reaction, 197
 Calabar beans, chemical examination, 285
 Calcagni, G., and L. Bernardini, basicity of organic acids containing alcoholic hydroxyls, 258, 252

- Calcium, alloys with magnesium, thallium, lead, copper, and silver, 53
and absolute alcohol, hydrogenation by, 137
atomic weight, 184, 190
estimation of small amounts by means of potassium permanganate, 171
chloride, analysis, 184, 190
fluoride, action on vanadium pentoxide, 233
Calculations, chemical and physical, reform of, 232
Callan, T., and F. B. Power. (See Power, F. B.)
Calorimeter, simplified combustion, 201
Cambil, L., amorphous silicon, 12
silicon sulphides, 12
Cambridge University, 121
Cameron, F. K., "Soil Solution" (review), 196
Campbell, D. F., progress in electro-metallurgy of iron and steel, 192
F. H., modified explosion eudiometer, 235
Camphane series, studies in, 278
Camphene, constitution, 267
oxidation with hydr. gen peroxide, 229, 237
Camphenylnitroamine, constitution, 278
Camphor, *a*-derivatives of, 301
ketone derivative of, 186
Camphorquinone, absorption spectra of isomeric hydrazones and semicabazones of, 242
Caoutchouc, vulcanisation by sulphur, apparent reversibility, 245
Carbamide, transformation of ammonium cyanate into, 287
Carbethyl group, probable cause of elimination as ethyl carbonate by action of sodium ethoxide, 268
Carbinols, alkyl and benzylpseudo-butylphenyl, dehydration, 118
asymmetric, 279
Carbon and nitrogen in organic compounds, determining, 228, 316
and other elements, influence on corrosion of steel, 142, 155
arc, occurrence of less reirangeable spectrum of cyanogen in, 276
cementation of iron by solid, 245
in steels, employment of combustion under pressure to determine, 197
iron and chromium, chemical and mechanical relations, 297
dioxide, action on bleaching powder, 265
in carbonates, use of sodium paratungstate in determination, 170
solubility in beer, 20
monoxide and chlorine, photochemical and thermal interaction, 242
estimation, 291
oxychloride, action on natural and artificial sulphides, 11
Carbonates, use of sodium paratungstate in determination of carbon dioxide in, 170
Cardiff, University College of South Wales and Monmouthshire, 124
Carnot, A., "Traité d'Analyse des Substances Minérales" (review), 58
Carvone, hydrogenation, 145
hydrosulphide, action of hydrogen cyanide on, 253
Casimiroa edulis seeds, constituents, 277
Caspari, F. and W. Biltz. (See Biltz, W.)
Castell-Evans, J., "Physico-chemical Tables" (review), 10
Catalysis, influence of foreign substances on activity of, 47
Catalysis, dehydrogenisation by, 318
of borneol, 108
Cathodic overvoltage, influence of physical condition of metals on, 316
Caven, K. M., "Systematic Qualitative Analysis" (review), 24
Cellulose from acetylcellulose, 202
Cement, 220, 290
setting of, 54
Cementite, magnetic transition temperature, 289
Cerium earth double sulphates, decomposition with alkali sulphates by fusion with charcoal, 179
method for separation, 61
separation by potassium permanganate, 210
Chablay, E., metallic alcohols, 306
use of liquid ammonia in chemical reactions, 293
Chamot, E. M., D. S. Pratt, and H. W. Redfield, phenolsulphonic acid method for determination of nitrates in water, 146, 159, 167, 178
Chapman, D. L., and F. H. Gee, photochemical and thermal interaction of chlorine and carbon monoxide, 242
and H. E. Jones, decomposition of dry ozone, 242
S., kinetic theory of a gas consisting of spherically symmetrical molecules, 16
W. G., "Continental Price Calculator" (review), 24
Charpy, G., and S. Bonnerot, cementation of iron by solid carbon, 245
gases contained in steel, 11
Chattaway, F. D., transformation of ammonium cyanate into carbamide, 287
C. L. Cumming, and B. H. Wildon, decomposition of hydrazides and hydrazones by heat, 21
and D. F. S. Wünsch, polymorphic phthalylhydrazides, 21
Chauvenet, E., action of carbon oxychloride on natural and artificial sulphides, 11
carbonates of thorium, 150
Chavanne, O., action of oxidising agents on isopropionic acid, 174
Chavaux, O., and J. Bougault. (See Bougault, J.)
Chelsea, South-Western Polytechnic, 135
Chemical change, conditions affecting, 175
constitution and residual affinity, relation between, 265
light actions, 60
qualification, professional, 134
Society, 7, 18, 228, 239, 246, 249, 265, 277, 285, 314
Address to King George V., 18
to University of St. Andrews, 18
report of International Committee on atomic weights, 218
Chemist, chances of the English, 292, 317
Chemistry and Physics, Congress of Pure and Applied, 294
Applied, Eighth International Congress of, 14
physical, applications to doctrine of immunity, 25, 39, 55
Chesneau, G., analysis of monazite sands, 197
Chikahigé, M., metallographic and photochemical investigations of the system sulphur and tellurium, 246
Chlopov, W., formation of oxidising agents in atmospheric air by ultra-violet rays, 162
Chloraloses, action of alkalis on, 47
of ammonia on, 71
Chlorides, acid, action on monosodium derivatives of benzyl cyanide, 72, 198
of Cu, Pb, Fe, Zn, Sn, and Bi, formation of compounds of, 210
of divalent metals, thermic analysis of binary mixtures of, 210
of K, Na, Hg, Pb, Cu, Zn, Sn, and Cd, binary systems of MgCl₂ and CaCl₂ with, 246
of monovalent elements, thermic analysis of mixtures of copper chloride with, 12
of monovalent metals, binary systems of, 12
thermic analysis of binary mixtures of, 120
Chlorination of aromatic compounds, relation of velocity of to constitution, 22
Chlorine, action on alkalis, 265
and carbon monoxide, photochemical and thermal interaction, 241
bromine and iodine, determination of ratio between, 212, 225
derivatives of benzene and toluene, absorption spectra, 240
derivatives of pyridine, 241
Chloroform narcosis, ventilation of lungs in, 264
Chlorourea, 245
Cholesterol in animal organisms, origin and destiny, 301
Chouchak, D., and I. Pouget. (See Pouget, I.)
Chouhri K. N., and H. Saha. (See Saha, H.)
Christopher, H., simple apparatus for sublimation in a vacuum, 251
and S. Smiles, synthesis of derivatives of thioxanthone, 280
Chromium, iron, and carbon, chemical and mechanical relations, 297
Chromotellurates, 72
Chromyl chloride, action on bornylene, 266
Clamician, G., and P. Silber, chemical light actions, 60
Cirencester, Royal Agricultural College, 127
Ciusa, R., and G. Scagliarini, researches on strychnine and brucine, 234
and A. Terni, action of hydroxylamine on ketones of the type R·CH:CH·CH:CH·CO·C₆H₅, 198
Clack, B. W., temperature coefficient of diffusion, 289
Clarke, F. W., annual report of committee on atomic weights, 5, 15, 28, 232
H. T., "Handbook of Organic Analysis, Qualitative and Quantitative" (review), 256
relation between residual affinity and chemical constitution, 265
and S. Smiles, synthesis of derivatives of thioxanthone, 230
Rosaling, and A. Senier. (See Senier, A.)
Claude, G., industrial manufacture of pure nitrogen, 282
luminescent neon tubes, 47
volatilisation of electrodes in neon tubes, 257
Clays, physical properties of, 290
Clayton, A., new coumarin derivatives, 265
and G. T. Morgan. (See Morgan, G. T.)
E. G., characteristics and chemical composition of some early matches, 223
Clerkenwell, Northampton Polytechnic Institute, 135
Clocks, pendulum, and their errors, 18
Coal, constituent of, 233
Cobalt and sodium oxalates, stability of double, 278
Cobb, V., G. P. Baxter, and T. Thorvaldson. (See Baxter, G. P.)
Cocker, R. B., diamonds, how and when they were made by nature, 248
Coffignier, C., properties of different varieties of dammar resin, 119
Cohen, E., allotropic forms of metals, 23
Cohnheim, O., "Chemie der Eiweisskörper" (review), 185
Coin, gold, counterfeit, 243
silver, composition of a false, 190
Coker, E. G., effects of holes and semicircular notches on distribution of stress in tension members, 254
and S. P. Thompson. (See Thompson, S. P.)
Colacicchi, U., action of aldehydes on pyrrol derivatives, 282
and G. Plancher. (See Plancher, G.)
Colin, H., and A. Sénéchal, action of acids on catalytic oxidation of phenols by ferric salts, 185
catalysing action of ferric sulphocyanide, 72
Collins, H., "Relative Volumes of the Atoms of Carbon, Hydrogen, and Oxygen when in Combination" (review), 161
Colloids, lecture on, 184
theory of, 139
Colombières-sur-Orb, radium emanation in gases from springs at, 293
Colour and constitution, 48
blindness and trichromatic theory of colour vision, 238
Colours, iridescent of birds and insects, 239
Colson, A., chromic sulphate and ions, 257
dissolved molecule and van't Hoff's hypothesis, 137
theory of solutions and heats of solutions, 293
Combustion calorimeter, simplified, 201
Comet, Halley's, spectroscopic proof of repulsion by sun of gaseous molecules in tail of, 85
Compounds, connection between volatility, fusibility, and density of, and chemical forces at play within their molecules, 29
definite, with varying composition of solid phase, 221
Condensations by ultra-violet light, 47
Condenser, improved Soxhlet, 54
Congro-red, osmotic pressure and conductivity of aqueous solutions of, 229
Constitution and colour, 48
utilisation of magnetic field for determining, 245
Cooper, A. (obituary), 103
W. K., Benko primary battery, 316
Copaux, H., constitution of metatungstates, 36
Copper and calcium alloys, 53
arsenic and antimony in, determination, 82, 91
colloidal, rate of coagulation, 139
electrolytic determination, 69
extraction of gases from, 185
heated in vacuo, extraction of gases from, 173
quantitative determination by means of hypophosphorous acid, 36
salts and their behaviour with alkalis, 266
water pipes, 96
chloride, mixtures with chlorides of monovalent elements, thermic analysis, 12
oxide, action of alkyl iodides on, 210
Cork, University College, 133
Corrosion Committee of British Association, report, 164

- Coste, J. H., E. T. Shelbourn, and E. K. Andrews, examination of petroleum mixtures, 305
- Cotarnine, condensation of condensation products, and condensation with aliphatic and aromatic nitrocompounds, 280
- Coumarin derivatives, new, 265
- Courtot, C., and V. Grignard. (See Grignard, V.)
- Couturier, F., catalytic dehydration of secondary and tertiary pinacolic alcohols, 258
- Cowper-Coles, S., announcement, 258
- Crémieu, V., and J. Danne. (See Danne, J.)
- Crites, B. O., determination of vanadium in steel and iron, 180
- Crossley, A. W., and G. F. Morrell, derivatives of orthoxylene, 315
- and Gertrude H. Wren, derivatives of orthoxylene, 315
- Crotonaldehyde condensation, 228
- Cryoscopy in fused sodium hyposulphite, 293
- Crystals, dehydration of, 252
- Cumming, A. C., notes on thermostats and devices used in connection therewith, 307
- "Practical Chemistry for Medical Students" (review), 221
- C. L. F. D. Chattaway, and B. H. Wilson. (See Chattaway, F. D.)
- Cuprignyllates, 21
- Cuzon, J. R., and J. N. Pring. (See Pring, J. N.)
- Cyanodihydrocarvone, stereo-isomeride of, 253
- Cyanogen, less refrangible spectrum of, and occurrence in carbon arc, 276
- Cyclohexane, bromination, 137
- Cyclohexanol and cyclohexanone, action of bromine on in presence of aluminium bromide, 186
- Cyclopentanone derivatives, 318
- D**ALMATIAN white thyme, essential oil of, 302
- Dammar resin, properties of different varieties, 119
- Danne, J., and V. Crémieu, radium emanation in gases from springs at Colombières-sur-Orb, 293
- Darling, C. R., experiments on surface tension, 254
- Darwin, F., and Miss D. F. M. Pertz, new method of estimating the aperture of stomata, 16
- Darzens, G., action of thionyl chloride on ethers of acid alcohols in presence of a tertiary base, 103
- new method of etherifying alcohols by hydrazides, 24
- and F. Bourion, action of thionyl chloride on metallic oxides, 135
- and H. Rost, synthesis of new hydroaromatic ketones, 282
- Datta, R. L., formation of dichlorocarbamide and its behaviour towards amines, 279
- Datura stramonium, D. fastuosa, and D. metel, active constituents, 266
- Davison, W., and J. N. Friend. (See Friend, J. N.)
- Dawson, H. M., and H. Ark, reactivity of ketones towards iodine, 241
- and May S. Leslie, ionisation in non-aqueous solvent, 228
- Day, A. L., recent advances in high-temperature gas thermometry, 51, 62
- and R. B. Sosman, melting-point of minerals in light of recent researches with gas thermometer, 221
- D'Albe, E. F., "Contemporary Chemistry" (review), 184
- De Boissaudran, L., and A. de Gramont, spectrum of beryllium and its bands in different sources of light, 186
- De Cesa is, P., binary system CuBr—KBr, 120
- systems: CuCl—AgCl, CuCl—NaCl, CuCl—KCl, 48
- and N. Parravano. (See Parravano, N.)
- De Coninck, G., and M. Raynaud, action of hydriodic acid on starch and dextrine, 137
- uranic dihydrate, 150
- De Forcrand, M., fluorhydrates of alkali fluorides, 72
- hydrates of rubidium and caesium fluorides, 11
- De Gramont, A., and L. de Boissaudran. (See de Boissaudran, L.)
- De Kolosovsky, N., influence of dissolved salts on partition of a substance between two solvents, 174
- De Luc, A., and F. Reverdin. (See Reverdin, F.)
- Dean, H. R., factors concerned in agglutination, 301
- Decacyclone and action on graphite, 12
- Decahydro- β -naphthol, two forms of, 258
- Deflocculation, 243
- Degrees, German University, 150
- Dehydrogenation by catalysis, 318
- Delacre, M., products of hydrolysis of raw and pure pinacone, 258
- quantitative dehydration of pure pinacone, 36
- Delépine, M., chlorides of iridium, 150, 246
- chlorosulphocarbonic ethers, 258
- pyridine pentachloroiridates, 47, 72
- pyridino-pentachloroiridates, 209
- pyridino-pentachloroiridates, 198
- sulpho-esters, R.CS. OR', 185
- thionic ethers, 258
- volatility of compounds containing sulphur, 257
- and R. Sornet, separation and determination of ammonia and pyridine, 198
- Denham, H. G., action of alkyl iodides on copper oxide, 210
- Denigès, G., modification of Malquin's reaction for characterisation of strychnine, 119
- new characteristic reaction of bromine, 119
- preparation of pseudomorphine by mineral catalysis, 36
- rapid method of determining nitrates and nitrites in water, 119
- Desgrez and Feuillie, M.M., determination of urea, 318
- Detouff, A., and A. Béhal. (See Béhal, A.)
- Dextrine, action of hydriodic acid on, 137
- Dey, B. H., and H. K. Sen, action of hydrazine sulphate on nitrites and a new method of determining nitrogen in nitrites, 210
- Diamonds, how and when they were made by nature, 248
- 2, 6-Dibenzoyl-2, 6-dimethylheptane, 84
- 2:2'-Dibromodiphenyl, 240
- Dichlorocarbamide, formation and behaviour towards amines, 279
- 2:2'-Dichlorodiphenyl, 240
- Dicyanin, 96
- Dieckmann, T., and S. Hilpert. (See Hilpert, S.)
- Diefenthaler, O., and E. Müller. (See Müller, E.)
- Diethylcyclohexadiene, synthesis from phenol, 286
- Diffusion, temperature coefficient of, 289
- Dihydrate, uranic, 150
- Dihydrocinnamylcarbamide, 228
- Dihydroxydihydrindamine and its resolution into optically active components, 273
- 1:4-Dihydroxy-2-thioxanthone, 230
- Diisobutylamine, action on α -bromobutyric acid, 84
- Diketones, β -substituted, synthesis by means of sodium ketones, 173
- β -Ketones, method of obtaining, 59
- 4:6-Dimethoxy-2- β -methylaminobenzaldehyde, synthesis, 21
- Dimethylbenzoylacetate ether, oximes and phenylalkylisoxazolones obtained with, 59
- Dimethyl-3, 4-dioxybenzylamine, 294
- Dimethylparaoxybenzylamine, 246
- Dimethylparatoluidine, absorption spectra of nitration products of, 250
- Dimethylpentene, 174
- Dinaphthothiophene, 11
- Dinitrohydroquinone, constitution of monomethylether of Weselsky and Benedikt's, 294
- 3, 6-Dinitroorthoxylene, 315
- Dinitroorthoxylidenes, 315
- Dioxide, new type of, 12
- 2, 3 and 3, 4-Dioxybenzylamines, 274
- Dipentene nitrosoazide, 22
- Diphenylquinone derivatives, 242
- Diphenylcarbamylloximes, 252
- Dispersion, optical, 249
- Distillation of binary mixtures of metals in metals in vacuo, 276
- Dialphides, aromatic of type R.S.R'.S.R' and R.S.R'.S.R', formation, 294
- 2:2'-Ditoly derivatives, formation of six- and seven-membered rings from, 279
- Ditrich, M., titration of ferrous oxide in silicates by Pebal-Dölter's method, 47
- Divalolactone, constitution, 197
- Dixon, H. B., presentation of Faraday medal to Prof. Richards, 9
- Dobbie, J. J., J. J. Fox, and A. J. H. Gauge, 2:2'-dibromodiphenyl and 2:2'-dichlorodiphenyl, 240
- Dodgson, J. W., stability of double oxalates of sodium and nickel, and sodium and cobalt, 278
- Donnan, F. G., and A. B. Harris, osmotic pressure and conductivity of aqueous solutions of Congo-red, and on reversible membrane-equilibria, 229
- and J. S. Thomas, solubility of cuprous oxide in aqueous ammonia solutions and composition of cuprous-ammonia complex, 230
- and A. S. White, the system: palmitic acid-sodium palmitate, 239
- Douetteau, R., 2, 3 and 3, 4-dioxybenzylamines, 274
- Douris, R., hydrogenation of crotonic aldehyde in presence of nickel, 294
- Dreaper, W. P., theory of dyeing, 265
- Dublin, Royal College of Science, 134
- University, 122
- Duffour, A., tridotetrachloro-oxalates and tetrachloroiridates, 47
- new types of trioxalic acids and complex trioxalates, 72
- Dumesnil, P., preparation of some asymmetric benzylalkyl acetic acids, 173
- Dundee, University College, 151
- Dunn, F. P., diphenylcarbamylloximes, 252
- Dunn, J. T., purifying mercury in the laboratory, 211
- Dunoyer, L., fluorescence of vapours of alkaline metals, 156
- Dunstan, A. E., and F. B. Thols, preparation of syn-aldoximes, 259
- W. R., and J. R. Hill, aerial oxidation (rusting) of metals, 241
- passivity of iron and other metals, 241
- Dupont, G., catalytic isomerisation of acetylenic pinacone, 59
- preparation of substituted ketohydrofurans, 185
- and W. Louguinine. (See Louguinine, W.)
- Dupuy, R. L., and P. Jolibois. (See Jolibois, P.)
- Durham University, 128
- Duval, H., molecular refraction of azo-compounds, 293
- Dye, root of, azarcan, 11
- Dyeing, role of affinity in, 36
- theory of, 265
- Dynamic isomerism, 140
- Dysprosium compounds, 60
- E**ARTHS, rare, compounds, 177
- East Ham Technical College, 136
- Easterfield, T. H., and Clara M. Taylor, preparation of ketones of higher fatty acids, 287
- Easton, R. F., and G. C. Jones. (See Jones, G. C.)
- Ebler, E., and M. Fellner, preparation of colloidal silicic acid, 161
- and R. L. Krause, zinc peroxyde (zinc monoxide, zinc peroxides), 162
- Edinburgh, Heriot-Watt College, 132
- University, 132
- Egerton, A. C., Hofmann's method for determination of vapour densities, 259
- A. C. G., addition to the Buchner funnel, 20
- Eichengrün, A., cellulose from acetylcellulose, 203
- Electric discharge, afterglow and kindred phenomena, 231
- stress between two unequal spherical electrodes, maximum value, 288
- Electro-analysis, 141
- Electro-chemistry of solutions in acetone, 283
- Electrode, ammonium, 253
- Electrodes, maximum value of electric stress between two unequal spherical, 288
- volatilisation in neon tubes, 257
- Electrolytes, influence of inactive on optical activity of l-malic acid in aqueous solution, 242
- Electro-metallurgy of iron and steel, progress in, 192
- Element, discovery of new, probably of platinum group, 283
- Elements, fundamental properties of, 7
- melting-points of chemical, 165
- the sulphides of which are precipitated by H₂S in acid solution, detection, 245
- which form insoluble sulphates, qualitative detection, 284
- Eller, W., and B. Emmert. (See Emmert, B.)
- Elliot, T. G., volumetric estimation of sulphur in iron and steel, 298
- Ellis, G. W., and J. A. Gardner, origin and destiny of cholesterol in animal organisms, 301
- Ellis, R., properties of oil emulsions, 17
- Emich, F., "Lehrbuch der Mikrochemie" (review), 95
- Emmert, B., and W. Eller, iodine-ester compounds, 233

- Engler, C., "Über Zerfallprozesse in der Natur" (review), 306
- Equation, Kirchhoff's, application to solutions, 241
- Equilibria with lead carbonate precipitates, 222
- Equilibrium $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + \text{Na}_2\text{SO}_4$, 162
- Ergothioneine, constitution, 315
- Ester, cinnamic acid, and cinnamic acid, complex mercury compounds of, 47
- Esters, hydroxy, action of phosphorus pentachloride and thionyl chloride on optically active, 250
- α -ketonic, lactonisation, 173
- Estreicher, T., purifying mercury in the laboratory, 269
- Ether salts, action on mono-sodium benzyl chloride, 174
- of acids of formic acid series, catalytic preparation, 84
- photolysis by ultra-violet rays, 197
- synthesis of ketonic by means of sodium ketones, 173
- use in metallic analysis, 60
- Ethers, anthranilic, chlorinated and brominated, 137
- chlorosulphocarbonyl, 258
- enolic, synthesis by means of sodium ketones, 173
- nitric, determination, 36
- of acid alcohols, action of thionyl chloride on in presence of a tertiary base, 118
- of dithiocarbonalkylamine acids, 306
- oxygen of, basic properties, 119
- thionic, 258
- Ether oxides, photolysis by ultra-violet rays, 197
- Etherification, catalytic, of aromatic acids, 137
- of dibasic acids, 283
- Ethyl derivatives of acetone, 72
- carbonate, probable cause of elimination of a carboethoxy group as, by action of sodium ethoxide, 263
- citratecon, condensation with ethyl sodiomalonate, 288
- ether, oximes and phenylalkylisoxazolones obtained with, 59
- sodiummalonate, condensation of ethyl citraconate with, 283
- Ethylene diammonium, halogen aurates of, 48
- Eudiometer, explosion, 235
- Euler, H., "Allgemeine Chemie der Enzyme" (review), 118
- Europium, 163
- Everest, A. E., molecular configuration of 1-methylcyclohexylidene-4-acetic acid and of oxime of cyclohexanone-4-carboxylic acid, 302
- and H. McCombie, effect of heat on a mixture of benzaldehyde-cyanohydrin and aniline, 240
- formation of glyoxalines from acyl derivatives, of α -keto- β -anilino- $\alpha\beta$ -diphenylethane, 229
- Ewins, A. J., derivatives of 4(or 5)-methylglyoxaline, 278
- synthesis of damascenic acid, 286
- and G. Berger. (See Berger, G.)
- Explosion eudiometer, 235
- Eye, sensibility to variations of wave-length, 18
- Eyoun, L., and J. H. Lane, determination of furfural by means of Fehling's solution, 304
- FACTORY and Workshop Act, 1901, regulations for smelting materials containing lead, &c., 162
- Fairlie, D. M., and J. N. Pring. (See Pring, J. N.)
- Faraday lecture, 7
- Medal, presentation to Prof. Richards, 8
- Society, 9, 22, 222, 268, 316
- Fats, melting-points of, Wiley method for determining, 15
- Fatigue tester, high-speed, 277
- Faucou, A., and G. Massol. (See Massol, G.)
- Fay, I. W., "Chemistry of the Coal-tar Dyes" (review), 208
- Fedorow, A. S., and G. J. Petrenko. (See Petrenko, G. J.)
- Feiser, J. P., and F. A. Gooch. (See Gooch, F. A.)
- Fellner, M., and E. Ebler. (See Ebler, E.)
- Fermentation, alcoholic, mechanism of, 173, 294
- Ferrario, E., phenoxthine, 119
- Ferric chloride and antipyrine compounds, 246
- Ferrocyanides, constitution of organic, 229
- Ferromagnetic compounds of manganese, 235
- Féry, C., stellar pyrometry, 10
- refractometer, 70
- Feuilié and Desgrez, M. (See Desgrez, M.)
- Fichtenholz, A., and E. Bourquelot. (See Bourquelot, E.)
- Findlay, A., "Phase Rule and its Applications" (review), 58
- and B. Shen, solubility of carbon dioxide in beer, 20
- Fink, C. G., ductile tungsten and molybdenum, 34
- Finnish turpentine, examination, 243
- Firth, J. B., dehydration of crystals, 252
- Fischer, F., and E. Tiede. (See Tiede, E.)
- M. H., "Das Ödem" (review), 149
- Fish, cooking and chemical composition of English, 271
- Fitzpatrick, R. M., estimation of water in soap, 247
- Flack, M., and L. Hill. (See Hill, L.)
- Flat surfaces, adherence of, 276
- Flint implements, discovery of novel type, 264
- Florentin, D., and M. Marquoyrol. (See Marquoyrol, M.)
- Flour, wheat, points concerning treatment of, 117
- Fluids, mechanical viscosity of, 17
- Fluorhydrates of alkali fluorides, 72
- Fluorene, magnesium derivative of, 59
- Fluorescence of vapours of alkaline metals, 186
- Fluorescent substances, propagation of light in, 306
- Fluorides, detection, 296
- Fluorine determination, quantitative, 35
- Fluosilicates, detection, 296
- Foods, tin in canned, determination, 66
- Forces, electromotive, in alcohol, 22, 205
- Formanek, J., and E. Grandmoulin, "Untersuchung und Nachweis Organischer Farbstoffe auf Spektroskopischen Wege" (review), 149
- Forster, M. O., new organic compounds of nitrogen, 236, 248
- and H. Stötter, dihydrocinamenylcarbamide (β -phenyl-ethyl-iso-cyanate), 228
- J. K. Trotter, and J. Weintraube, studies in camphane series, 278
- and F. M. van Gelderen, triazogroup, 22
- Fouard, E., preparation of semi-permeable membranes, 174
- Fouassio, A., and E. Bourgeois. (See Bourgeois, E.)
- Fournau, E., salts and ethers of alkylamino-dithiocarbonic acids, 119
- and M. Vila, salts and ethers of dithio-carbonalkylamino acids, 306
- Fowler, A., and H. Shaw, less refrangible spectrum of cyanogen, and its occurrence in carbon arc, 276
- and R. J. Strutt, spectroscopic investigations in connection with active modification of nitrogen, 276
- Fox, J. J., J. J. Dobbie, and A. J. H. Gauge. (See Dobbie, J. J.)
- Fractionation of yttrium earths by means of succinates, 203
- Franke, A., and R. Pribram. (See Pribram, R.)
- Frankland, E. P., action of benzylamine on 5-dibromosuccinic acid, 228
- method of determining carbon and nitrogen in organic compounds, 228, 316
- P. F., presentation of Faraday medal to Prof. Richards, 8
- Fraps, G. S., effect of ignition on solubility of soil phosphates, 191
- Freoch, A. G., discovery of new element, probably of platinum group, 283
- Freundler, P., benzeneaz xyorthobenzoic acid, 193
- chlorinated and brominated anthranilic ethers, 137
- constitution of oxyindazols, 209
- oxyindazols, 137
- preparation of ortho-substituted azoic acids, 174
- of oxyindazols from unsubstituted azoic or hydrazoic acids, 198
- researches on oxyindazols, 11
- Freundlich, H., theory of colloids, 139
- Friedel and Crafts' reaction, preparation of α -naphthalenic ketones by, 197
- Friend, J. N., "Corrosion of Iron and Steel" (review), 184
- report of corrosion committee of British Association, 164
- and W. Davison, composition of a false silver coin, 190
- Fruit of Solanum dulcamara, study of, 2
- Funnel, Buchner, addition to, 23
- improved, 30, 211, 312
- support, 30, 211
- Furfural, determination by means of Fehling's solution, 304
- Furfural hydrazones, phototropism of, 258
- Furnace, electric, product, 268
- electrolytic, method for producing metals, 45
- Fusion experiments with bisilicates, 48
- heat of substance melting in neighbourhood of ordinary temperature, 36
- Fusions, 190
- GABBI, G., and G. Poma. (See Poma, G.)
- Galway, University College, 134
- Gams, A., and A. Pictet. (See Pictet, A.)
- Gardner, J. A., and G. A. Buckmaster. (See Buckmaster, G. A.)
- and G. W. Ellis. (See Ellis, G. W.)
- Garrett, A. E., "Advance of Photography; its History and Modern Applications" (review), 305
- Gas constituted of spherically symmetrical molecules, kinetic theory of, 16
- distributor, movable, 247
- pressure regulators, forms of, 3
- Gases contained in steel, 11
- evolved by walls of glass and porcelain tubes, 59
- extraction from copper, 185
- heated in vacuo, 173
- from springs at Colombières-Orb, radium emanation in, 293
- Gastric juice, action on lead and mercury, 251
- Gaudechon, H., and D. Berthelot. (See Berthelot, D.)
- Gauge, A. J. H., J. J. Dobbie, and J. J. Fox. (See Dobbie, J. J.)
- Gault, H., lactonisation of α -ketonic esters, 173
- and E. E. Blaise. (See Blaise, E. E.)
- Gauthier, D., synthesis of tertiary α -ketonic alcohols, 11
- Gazarian, G. T., general relation between physical properties of substances, 293
- Gee, F. H., and D. L. Chapman. (See Chapman, D. L.)
- Gehrcke, E., "Über die Anwendung der Zylinderlinse in Spektralapparaten" (review), 71
- and O. Reichenheim, "Über das Doppelspektrum der Wasserstoffkanalstrahlen" (review), 71
- Geibel, W., electrical and mechanical properties of alloys of noble metals, 36
- German university degrees, 150
- German silver and other alloys, nickel-zinc separation in, 58
- Gillette, C. E., effect of continued grinding on water of crystallisation, 313
- Girard, P., and V. Henri, new hypotheses of molecular state of substances in solution, 306
- Glasgow and West of Scotland Technical College, 132
- Glass tubes, gases evolved by walls of, 59
- Glätzel, E., potassium barium orthosulphatimonate, 244
- orthosulphareneate, 209
- Glucinum and its bands, spectrum in different sources of light, 186
- α -Glucodecose and glucodecite, 118
- Glucoside in leaves of pear trees, 197
- saponarin, adsorption of iodine by, 139
- Glycerol determination, report on method, 46
- Glycollaldehyde, bimolecular, 242
- Glyoxydines, formation from acyl derivatives of α -keto- β -anilino- $\alpha\beta$ -diphenylethane, 229
- Godbole, N. N., reduction of silver chloride, 173
- Godchot, M., hexahydrohippuric acid, 36
- and F. Laboury, derivatives of cyclopentanone, 318
- Gold, coefficients of magnetisation, 174
- coin, counterfeit, 243
- quantitative determination by means of ether, 35
- Goldbaum, J. S., determination of ratio between chlorine, bromine, and sodium, 212, 225
- Gooch, F. A., determination of silver by electrolytic separation from ammoniacal oxalate solution, 36
- and C. N. Boynton, separation and determination of barium in presence of calcium and magnesium, 48
- and J. P. Feiser, estimation of silver by electro-deposition from an ammoniacal solution of the oxalate, 93
- and S. B. Kuzirian, use of sodium paratungstate in determination of carbon dioxide in carbonates and nitrogen pentoxide in nitrates by loss on ignition, 170
- Goulding, E., and R. G. Pelly, note on paramethoxyacylaldehyde and its occurrence in root of chlorocodon, 251
- Goutal, E., and P. Mahler. (See Mahler, P.)

- Grandmougin, E., and J. Formanek. (See Formanek, J.)
- Graphite, action of decacyclone on, 12
- Green, A. G., and E. A. Bearder, alkaline condensations of nitrohydrozo-compounds, 25
- J. W., chances of the English chemist, 318
- Greenwood, H. C., boiling points of metals, 31, 42
- Griffiths, W., "Principal Starches used as Food" (review), 184
- Grignard, V., and C. Courtot, magnesium derivative of fluorene, 59
- Guichard, M., extraction of gases from copper and the determination of oxygen, 185
- from copper heated in vacuo, 173
- gases evolved by walls of glass and porcelain tubes, 59
- Gulick, L. M. A. Rosanoff, and H. K. Larkin. (See Rosanoff, M. A.)
- Gum kino, reactions of, 22
- Gutbier, A., and C. J. Obermaier, halogen aurates of ethylene and propylene diammonium, 48
- HACKSPILL, L.**, preparation of alkaline metals, 59
- and Broniewski, M. M. (See Broniewski, M.)
- Hadfield, Sir R., metallurgy, 13
- Sinhalese iron of ancient origin, 275
- Hall, W. T., and R. S. Williams, "Introduction to Chemistry" (review), 35
- Hailer, A., and E. Bauer, 2, 6-Dibenzoyl-2, 6-dimethylheptane and $\alpha\alpha'$ -tetramethylpimelic acid, 84
- ketones of type of benzyldimethylacetophenone, 150
- oximes and phenylalkylisoxazolones obtained with ethyl, methyl, and dimethylbenzoylacetate ethers, 59
- synthesis of β substituted diketones, ketonic ether salts, and enolic ethers by means of sodium ketones, 173
- Halley's comet, repulsion by sun of gaseous molecules in tail, 85
- Halogens, adsorption by dry slaked lime, 316
- Hancock, W. C., physical properties of clays, 290
- Hanriot, M., and A. Kiling, action of alkalis on chloraloses, 71
- of ammonia on chloraloses, 47
- and F. Raoult, coefficients of magnetisation of gold, 174
- Hansen, C. J. T., reform of chemical and physical calculations, 232
- Hanus, J., and O. Kallauner, action of hydrogen peroxide and sodium peroxide on bismuth salts, 36
- and A. Soukup, quantitative determination of copper by means of hypophosphorous acid, 36
- Harcourt, A. G. V., and H. B. Baker, alleged complexity of tellurium, 19, 260
- Harden, A., and S. G. Paine, action of dissolved substances upon the autofermentation of yeast, 301
- Harding, V. J., substitution in aromatic hydroxy-compounds, 230
- Hardman, R. T., and A. Lapworth, electromotive forces in alcohol, 265
- and J. R. Partington, application of Kirchhoff's equations to solutions, 241
- Harker, J. A., high-temperature equipment of the National Physical Laboratory, 9
- Harlow, F. J., cubical expansion of fused silica, 289
- Harmonograph, 255
- Harris, A. B., and F. G. Donnan. (See Donnan, F. G.)
- Hart, E., "Chemistry for Beginners" (review), 71
- Hartley, E. G. J., constitution of the organic ferrocyanides, 229
- Hasenfratz, V., and A. Arnaud. (See Arnaud, A.)
- Hatschek, E., lecture on colloids, 184
- Havelock, T. H., influence of solvent on position of absorption bands in solutions, 249
- optical dispersion, 249
- Heat, effect on a mixture of benzaldehydecyanohydrin and aniline, 249
- Heath, G. L., determination of arsenic and antimony in copper, 82, 91
- Hébert, A., composition of oil-seeds from French West Africa, 174
- decomposition by heat of metallic xanthates, 119
- Heilbron, I. M., and G. G. Henderson. (See Henderson, G. G.)
- and G. B. Neave. (See Neave, G. B.)
- Heinzelmann, A., and O. Ruff. (See Ruff, O.)
- Henderson, G. G., and R. Boyd, contributions to chemistry of terpenes, 286
- and I. M. Heilbron, constitution of camphene, 267
- contributions to chemistry of terpenes, 266
- and Maggie M. J. Sutherland, contribution to chemistry of terpenes, 229
- oxidation of camphene with hydrogen peroxide, 287
- Henri, V., influence of various physical conditions on ultraviolet radiation of quartz mercury lamps, 197
- ultra-violet radiations of quartz mercury lamps, 185
- and P. Girard. (See Girard, P.)
- Henriot, E., radiation of rubidium, 47
- Herbage studies, 276
- Herrmann, G., formation of compounds of chlorides of Cu, Pb, Fe, Zn, Sn, and Bi, 210
- Herschinkel, M., action of radium emanation on thorium salts, 163
- Herz, W., equilibria with lead carbonate precipitates, 222
- equilibrium $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + \text{Na}_2\text{SO}_4$, 162
- and A. Bulla, periodides and perbromides of metals of alkaline earths, 210
- Hexahydrobenzylamine, preparation, 174
- Hill, A. T., appointment, 261
- J. R., and W. R. Dunstan. (See Dunstan, W. R.)
- L., and M. Flack, physiological influence of ozone, 301
- Hilpert, S., and J. Beyer, ferrosulfuric oxide, 96
- and T. Dieckmann, ferromagnetic compounds of manganese with phosphorus, arsenic, antimony, and bismuth, 270
- iron and magnesium arsenides, 233
- Histidine, synthesis, 228
- Hodges, E. R., simple sulphuretted hydrogen apparatus, 189
- Hofmann's method for determination of vapour densities, 259
- Holle, H., and A. Reissert. (See Reissert, A.)
- Holmberg, O., holmium, 209
- Holmium, 209
- Holton, W. O. R., and A. Porritt, memorial to Dr. J. Priestley, 269
- Hönigschmid, O., and T. W. Richards. (See Richards, T. W.)
- Hooper, D., *Pleurotus cretaceus*, an Indian edible mushroom, 145
- Hope, E., condensation of ethyl citraconate with ethyl sodiummalonate, 288
- and R. Robinson, synthetical experiments in group of isocoumarins, 230
- Hopkinson, B., high-speed fatigue tester and endurance of metals under alternating stresses of high frequency, 277
- Hopwood, A., and C. Weizmann, synthesis of polypeptides of α -amino- n -nonoic acid with glycine, alanine, valine, leucine, asparagine, and aspartic acid, 230
- Horton, E., H. E. Armstrong, and E. F. Armstrong. (See Armstrong, H. E.)
- Howard, H., and F. G. Pope. (See Pope, F. G.)
- Huber, P., and E. Bourgeois. (See Bourgeois, E.)
- Hughes, E. C., and A. W. Titherley. (See Titherley, A. W.)
- Humphries, A. E., some points concerning the treatment of wheat flour, 117
- Hüttner, C., and F. Mylius. (See Mylius, F.)
- Hydrates, magnetic study of role of water in constitution of solid, 245
- Hydration of metaphosphoric acid, 221
- Hydrazides, decomposition by heat, 21
- Hydrazine sulphate, action on nitrites, 210
- Hydrazones and semicarbazones of camphorquinone, absorption spectra of isomeric, 242
- decomposition by heat, 21
- Hydroaromatic compounds, bromination in presence of aluminium bromide, 137
- substances, study of, 141
- Hydrocarbons, synthesis at high temperature, 239
- Hydrogen electrode in alcohol and influence of water on its electromotive force, 265
- in organic molecules, determination of active, 186
- tantalum and tungsten, 233
- Hydrogen arsenide, determination of solid, 36
- chloride, temperature-coefficient of electrical conductivity of, in alcoholic solution, 266
- cyanide, action on carvone hydroaldehyde, 253
- peroxide, action on bismuth salts, 36
- on oxygen compounds of iodine, 318
- formation by electric discharge, 293
- oxidation of camphene with, 229, 287
- Hydrogenation by calcium and absolute alcohol, 137
- by means of nickel and sodium hypophosphite, 119
- by precipitated palladium and sodium hypophosphite, 119
- catalytic, of camphor, 198
- in presence of divided palladium, 198, 209
- Hydroxide, thallous, 120
- Hydroxy-acids, action of phosphorus pentachloride and of thionyl chloride on, 250
- compounds, aromatic, substitution in, 230
- Hydroxyls, alcoholic, basicity of organic acids containing, 258, 282
- Hydroxylamine, action on ketones of type— $\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, 198
- IBBOTSON, F., note on the determination of nickel, 224
- Imino-compounds, formation and reactions, 240
- Immunity, applications of physical chemistry to doctrine of, 25, 39, 55
- Imperial College of Science and Technology, 123
- Indian edible mushroom, 145
- solaceous plants, active constituents, 266
- Indicators of methyl-red type, 228
- use for determining affinity values, 115
- Indigoid condensation, negative case of, 119
- Insects, iridescent colors of, 239
- Institute of Chemistry, 134, 220, 258, 290
- pass list, 60
- Inversion, Walden, experiments on, 250
- Iodine, action of hydrogen peroxide on oxygen compounds of, 318
- adsorption by glucoside saponaria, 139
- and bromine, extraction by chloroform and carbon disulphide, 119
- approximate estimation of starch by, 244, 271
- bromine and chlorine, determination of ratio between, 212, 225
- derivatives of benzene and toluene, absorption spectra, 257
- reactivity of ketone towards, 241
- solutions, colour of, 221
- in organic substances, equilibrium of, 12
- tin ester compounds, 233
- Iodo-compounds, relative activities of organic, 288
- Ionisation of non-aqueous solutions, 238
- Ionising radiations emitted by radium C, 84
- Ions and chromic sulphate, 257
- Ipomoea orizabensis, chemical examination of root of, 314
- Ireland, National University of, 134
- Iridium, electrical properties, 293
- chlorides, 150, 246
- Iridotetrachloro-oxalates, 47
- Iridoxalates, new type of, 72
- Iron and Steel Institute, 162
- Iron and magnesium arsenides, 209
- and manganese, quantitative separation, 257
- and other metals, passivity, 241
- and steel, colorimetric method for vanadium in, 194, 202
- and steel, determination of vanadium in, 180
- metalurgy, progress in, 192
- sulphur in, volumetric estimation, 298
- and vanadium present together, volumetric determination, 209
- as catalyst in synthesis of ammonia under pressure, 161
- atomic weight, revision, 48, 64, 79, 88, 113
- cementation by solid carbon, 245
- chromium and carbon, chemical and mechanical relations, 297
- flame spectrum and those of sunspots and lower-type stars, 275
- meteoric, atomic weight, 48, 113
- Sinhalese, of ancient origin, 275
- Isobutylamine, action on α -bromobutyric acid, 84
- Isomerisation, catalytic, of acetylenic pinacone, 59
- Isoprenes, preparation from terpene hydrocarbons, 186
- Isouquinoline derivatives, 239
- alkaloids, synthetical experiments in group of, 280

- JAGO, W., and W. C. Jago, "Technology of Bread-making" (review), 148
- JAMES, C., thulium, 73
- and L. A. Pratt, new method for separation of cerium, 61
- new rare earth compounds, 177
- and J. E. Robinson, europium, 163
- H. W., chances of the English chemistry, 318
- J. H., and J. A. Schaeffer, "Experiments for Engineering Students in General Chemistry" (review), 317
- T. C., β -chlorocinnamic acids, 239
- Jamieson, G. S., volumetric method for determining antimony in alloys, 81
- Jänecke, E., formation of conversion salt-petre from point of view of phase law, 119
- Jantsch, G., and A. Ohl, compounds of dysprosium, 60
- Japan wax, alcoholysis, 135
- Jeanneret, B., and M. Wunder. (See Wunder, M.)
- Jellinek, K., role of iron as catalyst in synthesis of ammonia under pressure, 161
- Johnson, A. E., recent developments of phenolsulphonic acid method for determination of nitrates in water, 235
- Johnston, J., and L. H. Adams, influence of pressure on melting-point of some metals, 221
- Jolibois, P., allotropic modifications and melting-point of arsenic, 118
- and E. L. Dupuy, definite compounds of arsenic and tin, 24
- Jones, G. C., and R. F. Easton, note on ground almonds, 305
- II. C., "Electrical Nature of Matter and Radio-activity," (review), 232
- H. E., and D. L. Chapman. (See Chapman, D. L.)
- H. O., and C. S. Robinson. (See Robinson, C. S.)
- Jourdain, P. R., "Manuel Pratique d'Analyse Organique" (review), 71
- Juritz, C. F., "Notes on the Fertilisers, Farm Foods, Seeds, and Pest Remedies Act (Cape Province)" (review), 35
- KALLAUNER, O., and J. Hanus. (See Hanus, J.)
- Kaye, G. W., and T. H. Laby, "Physical and Chemical Constants and some Mathematical Functions" (review), 281
- G. W. C., silica standard of length, 17
- Keane, C. A., "Technical Methods of Chemical Analysis" (review), 292
- Keegan, P. Q., notes on plant chemistry, 109
- Kenner, J., and Emily G. Turner, formation of six- and seven-membered rings from derivatives of 2,2'-ditolyl, 279
- Kernbaum, M., decomposition of water by metals, 84
- Keto acids, 137
- acrylic, 59
- Ketohydrofurans, catalytic preparation, 185
- Ketone derivative of camphor, 186
- Ketones, action on monosodium derivative of benzyl cyanide, 72
- aromatic, catalytic preparation, 294
- hydroaromatic, synthesis, 282
- in essential oils, quantitative determination, 169
- α -naphthalenic, preparation by Friedel and Crafts' reaction, 197
- Ketones of higher fatty acids. preparation, 287
- of type of benzylidimethylacetophenone, 150
- of type $R \cdot CH:CH \cdot CH:CH \cdot CO \cdot C_6H_5$, action of hydroxylamine on, 198
- reactivity towards iodine, 241
- Kinetic theory of a fourth state of matter, radio-activity as, 110
- King, H., chlorination of α -naphthol by acetylchloroamine-2,2-dichlorobenzene, 230
- and K. J. P. Orton. (See Orton, K. J. P.)
- Kipping, F. S., and W. H. Perkin, "Inorganic Chemistry" (review), 10
- Kirchhoff's equation, application to solutions, 241
- Klever, H. W., and H. Staudinger. (See Staudinger, H.)
- Kling, A., and M. Hanriot. (See Hanriot, M.)
- Knapp, A. W., and H. S. Shrewsbury. (See Shrewsbury, H. S.)
- Kobert's reaction as test for salicylic acid, 244
- Kohlschütter, V., and P. Sazanoff, metallic nitroso-compounds, 96
- Krauze, R. L., and E. Ebler. (See Ebler, E.)
- Kuntzer, H., and R. Meldola. (See Meldola, R.)
- Kurnakov, N. S., and W. J. Smirnow. (See Smirnow, W. J.)
- Kuzirian, S. B., and F. A. Gooch. (See Gooch, F. A.)
- LABAT, A., extraction of bromine and iodine by chloroform and carbonyl disulphide, 119
- Labradorite-norite with porphyritic labradorite crystals, 161
- Laby, T. H., and G. W. Kaye. (See Kaye, G. W.)
- Lactonisation of α -ketonic esters, 173
- Ladenburg, A., obituary, 117
- Lamps, quartz mercury, ultra-violet radiations, 185, 197
- Landau, M., action of ultra-violet rays on lactic acid, 24
- Lane, J. H., and L. Eynon. (See Eynon, L.)
- Landry, M., dinaphthothiophene, 11
- oxy- β -methylthiophenes, 293
- oxythiophenes, 162
- Lankester, Sir E. Ray, discovery of novel type of flint implements, 264
- Lankhshear, F. R., and A. Lapworth, absorption spectra of isomeric hydrazones and semicarbazones of camphor-quinone, 242
- Lapworth, A., and R. T. Hardman. (See Hardman, R. T.)
- and F. R. Lankhshear. (See Lankhshear, F. R.)
- and J. R. Partington, electromotive forces in alcohol, 22
- and V. Steele, new stereoisomeride of cyanodithiocarbamide, 253
- some reactions of phenylisopropyl ketone, 252
- Larkin, H. K., M. A. Rosanoff, and L. Gulick. (See Rosanoff, M. A.)
- Lavoux, J., action of methylene chloride on paraparaditolylmethane, 47
- Laws, E. G., and N. V. Sidgwick, isomeric acetaldehydephenylhydrazones, 279
- Le Bas, G., influence of alternating factor in certain series on molecular volumes at melting-point, 22
- of constitution of molecular volumes of organic compounds at boiling-point, 151, 166, 187, 199
- Lead, action of allium sativum or gastric juice on, 251
- and calcium, alloys, 53
- cadmium and bismuth alloys, binary and tertiary, 35
- regulations for smelting materials containing, 162
- carbonate precipitates, equilibria with, 222
- Leather formation, value of non-tannins in, 291
- Lebeau, P., formula of uranium carbide, 119
- Lebedeff, A., character of ymase, 177
- mechanism of alcoholic fermentation, 173, 294
- Lebedev, P., fusion experiments with bisulphides, 48
- Lederer, C., preparation of pure aromatic tellurium compounds, 233
- Leeds, Central Technical School, 135
- University, 127
- Léger, E., constitution of nitro derivatives obtained by the action of nitric acids on alols, 173
- of nitro-derivatives of alols, 258
- Lehmann, O., "Das Kristallisationsmikroskop und die Damit Gemachten Entdeckungen Insbesondere die der Flüssigen Kristalle" (review), 232
- "Die Neue Welt der Flüssigen Kristalle" (review), 149
- Length, silica standard of, 17
- Leslie, May S., molecular weight of thorium emanation, 186
- and H. M. Dawson. (See Dawson, H. M.)
- Lespieau, M., properties of monobrominated acrolein, 306
- Levy, L. A., estimation of carbon monoxide, 291
- Lewis, W. C. McC., compressibility of mercury, 115
- and A. Roshdestwensky. (See Roshdestwensky, A.)
- Ley, H., and K. von Engelhardt, colour of iodine solutions, 221
- Lickfett, H., and O. Ruff. (See Ruff, O.)
- Liebermann, C., root-dye of azafraan, 11
- Light actions, chemical, 60
- propagation in fluorescent substances, 306
- ultra-violet, condensations by, 47
- Lime, absorption of halogens by dry slaked, 316
- Limonene, hydrogenation, 84
- d*-Limonene nitrosoazide and *l*-limonene nitrosoazide, 22
- Liverani, R., and F. C. Palazzo. (See Palazzo, F. C.)
- Liverpool University, 128
- Lockyer, Sir J. N., iron flame spectrum and those of sun-spots and lower-type stars, 275
- Loquinn, R., α -methylaurenol, new ketone derivative of camphor, 136
- and P. Barbier. (See Barbier, P.)
- London, City and Guilds of, Institute, 60, 135
- City of, College, 135
- East, College, 136
- University, 121, 122
- Long, F. S., velocity of addition of alkyl bromides to cyclic tertiary bases, 302
- Loring, F. H., atomic weight of actinium, 59
- Losanitch, S., constitution of di-valolactone, 197
- Lotus corniculatus, a cyanophoric plant, 276
- Louguine, W., and G. Dupont, heat of fusion of substances melting in the neighbourhood of ordinary temperature, 36
- Low, W. H., precipitation of nickel compounds and preparation of spongy nickel, 244
- Lowell, P., spectroscopic proof of repulsion by sun of gaseous molecules in tail of Halley's comet, 85
- Lowry, T. M., and W. R. Bousfield. (See Bousfield, W. R.)
- Lucas, A., "Ministry of Finance, Egypt, Report on Work of Laboratories in 1910" (review), 209
- P., dehydration of alkyl and benzylpseudoisobutylphenyl carbinoles, 118
- Lunge, G., "Manufacture of Sulphuric Acid and Alkali" (review), 10
- "Technical Methods of Chemical Analysis" (review), 292
- Lunge, ventilation in chloroform narcosis, 264
- Luther, R., R. Abezg, and F. Auerbach. (See Abezg, R.)
- Lyman, J. A., and W. C. Morgan. (See Morgan, W. C.)
- M'CASE, C. R., a colorimetric method for vanadium in iron and steel, 134, 202
- McClelland, N. P., bimolecular glycolaldehyde, 242
- McCombie, H., and A. E. Everest. (See Everest, A. E.)
- McCrae, J., Kobert's reagent as a test for salicylic acid, 244
- Machine for computing percentages of materials comprising a mixture, 227
- McKenzie, A., and F. Barrow, experiments on Walden inversion, 250
- MacMahon, Major P. A., memoir on theory of partitions of numbers, 16
- McRae, J. A., and W. O. Walker. (See Walker, W. O.)
- Magnesium and calcium alloys, 53
- and iron arsenides, 233
- and zinc compound, isolation, 276
- derivative of fluorene, 59
- Magnetic field, utilisation for determining constitution, 245
- to determine composition, 257
- Magnetisation of gold, coefficients of, 174
- Mahler, F., and E. Goutal, employment of combustion under pressure to determine carbon in steels, 197
- Mai, J., sulphur phosphorus compounds, 60
- syntheses with yellow phosphorus, 161
- Maille, A., and M. Murat, catalytic reduction of cyclic oximes, 59
- and P. Sabatier. (See Sabatier, P.)
- Maiaquin's reaction for characterisation of strychnine, modification, 119
- Malefern, 305
- Mallock, H. R. A., iridescent colours of birds and insects, 239
- pendulum clocks and their errors, 18
- Malvern, P., determination of tannin in wine, 138
- Manchester Municipal School of Technology, 136
- University, 129
- Manganese and iron, quantitative separation, 257
- and thallium alloys, 53
- determination by sodium bis-muthate method, 94
- ferromagnetic compounds, 233
- compounds with phosphorus, arsenic, antimony, and bismuth, 270
- Maoz, H., and W. Prandtl. (See Prandtl, W.)
- Marcus, E., and W. Biltz. (See Biltz, W.)
- Marino, L., and C. Porlezza, luminosity of phosphorus, 12

- Marino, L., and V. Squintani, existence of new type of dioxide, 12
- Marqueyrol, M., and D. Florentin, Determination of nitrates and nitric ethers, 36
- Maraden, E., and T. Barratt, α -particles emitted by active deposits of thorium and actinium, 289
- Effie G., and S. Smiles, synthesis of derivatives of thioxanthone from aromatic disulphides, 238
- Marsh, J. E., α -derivatives of camphor, 301
- Marshall, H., notes on thermostats, 295
- Martegiani, E., and G. Bargellini. (See Bargellini, G.)
- Martin, G., connection between volatility, fusibility, and density of compounds, and chemical forces at play within their molecules, 29
- "Triumphs and Wonders of Modern Chemistry" (review), 58, 137
- Martindale, W., "Winter Specialties" (review), 244
- Mascarelli, L., two forms of decahydro- β -naphthol, 258
- Massol, G., and A. Faucon, latent heat of fusion and specific heat of fatty acids, 185
- Matches, characteristics and chemical composition of early, 223
- Matignon, C., presence of zinc nitrate in zinc powder and in commercial zinc, 24
- Matter, radio-activity as a kinetic theory of a fourth state of, 110
- Matthews, R. B., announcement, 182
- May, P., "Chemistry of Synthetic Drugs" (review), 71
- Meldola, R., and H. Kuntzen, synthesis with phenol derivatives containing a mobile nitro-group, 279
- Meldrum, A. N., development of atomic theory, 37, 49
- substances related to cochenillic and carminic acids, 239
- Melting-points of chemical elements, 164
- Membrane-equilibria, reversible, 229
- Membranes, preparation of semipermeable, 174
- Meneghini, D., and G. Bruni. (See Bruni, G.)
- Menge, O., binary systems of $MgCl_2$ and $CaCl_2$ with chlorides of K, Na, Hg, Pb, Cu, Zn, Sn^{+} , and Cd, 246
- Mennicke, H., "Die Metallurgie des Wolframs" (review), 292
- Menthadiene, synthesis from thymol, 286
- Mercury, action of allium sativum or gastric juice on, 251
- compounds of cinnamic acid ester and cinnamic acid, 47
- compressibility, 115
- purifying in laboratory, 149, 221, 269
- thread in a glass tube, resistance to motion, 276
- Metals action of sulphuryl chloride on, 174
- aerial oxidation (rusting), 241
- allotropic forms of, 23
- boiling-points of, 31, 42
- distillation of binary compounds of, in metals in vacuo, 276
- electrical and mechanical properties of alloys of noble, 36
- electrolytic furnace method for producing, 45
- endurance under alternating stresses of high frequency, 277
- formation of solid solutions of, by diffusion in solid state, 186
- influence of physical condition of, on cathodic overvoltage, 316
- Metals, influence of pressure on melting-points, 241
- Metallic analysis, use of ether in, 60
- Metallography of system of selenium-antimony, 186
- Metallurgy, 13
- Metainitrobenzoylparaanisidine, nitration, 185
- Metatungstates, constitution, 36, 48
- Methoxyepinaphthhyrindone, 277
- Methyl acetylpyrotartrate, action of organo-magnesium compounds on, 198
- alcohol, determination of small quantities, 305
- α -Methylaurenone, 186
- Methyl ether, oximes and phenylalkylisoxazolones obtained with, 59
- (4 or 5)-Methylglyoxaline, derivatives, 278
- α -Methyl indol, oxidation, 13
- Methyl ketones, synthesis, 198
- Methyl-red type, indicators of, 228
- Methylene chloride, action on paraparaditylmethane, 47
- Meunier, J., conditions of production of Swan spectrum, 293
- Meyer, A., azomethines derived from phenylisoxazolone, 84
- R. J., detection and determination of thorium with iodic acid, 120
- Micklethwait, Frances M. G., and G. T. Morgan. (See Morgan, G. T.)
- Milk, composition of Australian, 305
- of sweetened condensed, 305
- cow's, peroxyladiastase of, and paraphenylenediamine reaction, 36
- phosphorus in, gravimetric estimation, 244
- Miller, E. H., aldehyde figure of butter, 305
- composition of Australian milk, 305
- of sweetened condensed milk, 305
- gravimetric estimation of phosphorus in milk, 244
- Millington, J. P., "Modern Industrial Chemistry" (review), 149
- Mine rescue apparatus, 6
- Minerals, melting-point, 221
- Mint, Royal, annual report, 263
- Mitchell, C. A., copper water pipes, 96
- Moir, J., new derivatives of diphenylquinone and a new variety of stereoisomerism, 242
- Molecular configuration of 1-methylcyclohexylidene - 4-acetic acid and of oxime of cyclohexanone - 4-carboxylic acid, 302
- refraction of azo-compounds, 293
- state of substances in solution, new hypotheses of, 306
- volumes at melting-point, influence of alternating factor on, 22
- of organic compounds at boiling-point, influence of constitution on, 151, 166, 187, 199
- weight of thorium emanation, 186
- Molecule, dissolved, and van't Hoff's hypothesis, 137
- Molecules, determination of active hydrogen in organic, 186
- Molybdenum and nickel alloys, 53
- ductile, 34
- Monazite sands, analysis, 197
- Monomethyl - 3, 4-dicybenzylamine, 294
- Monomethylether of Weselsky and Benedikt's dinitrohydroquinone, constitution, 294
- Monomethylparaoxybenzylamine, 246
- Monosodium derivative of benzyl cyanide, action of acid chlorides, acid anhydrides, and ketones on, 72
- of aromatic acetones on, 209
- benzyl cyanide, action of acid chlorides and anhydrides on, 198
- of ether salts on, 174
- Montgomerie, H. H., and T. S. Patterson. (See Patterson, T. S.)
- Morgan, G. T., and A. Clayton, absorption spectra of nitration products of dimethylparatoluidine, 250
- and Frances M. G. Micklethwait, organic derivatives of antimony, 285
- W. C., and J. A. Lyman, "Chemistry" (review), 231
- Morochowetz, L., "Verhalten des Globulins zu den Saurativen Acidogloblin" (review), 71
- Morrell, G. F., and A. W. Crossley. (See Crossley, A. W.)
- Morrison, J. S., chances of the English chemist, 292
- Moureu, C., and J. C. Bongrand, propylic compounds, cyanacetylene, 24
- and A. Valeur, spartein, 59
- Müller, E., and O. Diefenthaler, volumetric determination of iron and vanadium present together, 209
- Murat, M., and A. Mailhe. (See Mailhe, A.)
- Museum, technical, in Vienna, 84
- Mushroom, Indian edible, 145
- Mushrooms, lactic acid obtained from, 232
- Mylius, F., quantitative determination of gold by means of ether, 35
- and C. Hüttner, use of ether in metallic analysis, 60
- Myrica Gale, L., composition of essential oil of, 241
- Myricetin, 242
- α -NAPHTHOL, chlorination by acetylchloroamino-2:4-dichlorobenzene, 280
- Naphthylidene-amines, 278
- Nash, L. M., examination of Finnish turpentine, 243
- National Physical Laboratory, high-temperature equipment of, 9
- Neave, G. B., and I. M. Heilbron, "Identification of Organic Compounds" (review), 244
- Nelson, E. K., quantitative determination of ketones in essential oils, 169
- Neogi, P., preparation of nitrites of primary, secondary, and tertiary ammonium bases, 253
- trialkylammonium nitrites and nitrites of bases of pyridine and quinoline series, 228
- Neon tubes, luminescent, 47
- volatilisation of electrodes in, 257
- Neoxyberberine, 239
- Nernst, W., and H. T. Tizard, "Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics" (review), 196
- Newcastle-on-Tyne, Armstrong College, 128
- Nickel and molybdenum, alloys, 53
- and sodium hypophosphite, hydrogenation by means of, 119
- and sodium oxalates, stability of double, 278
- and zinc alloys, 257
- compounds, precipitation, and preparation of spongy nickel, 244
- determination, 224
- in steel, comparison of methods for determination, 163
- superoxide, 246
- Nickel-zinc, separation in German silver and other alloys, 58
- Nicol, J., and C. G. Barkla. (See Barkla, C. G.)
- Nicolas, E., peroxyladiastase of cow's milk and the paraphenylenediamine reaction, 36
- Niton, action on salts of thorium, 175
- Nitrate and nitrite assimilation, 47
- mercurous, action of ammonia on, 210
- Nitrates and nitrites in water, determining, rapid method, 119
- determination, 36
- in water, determination, phenolphosphonic acid method, 146, 159, 167, 178, 235
- nitrogen pentoxide in, use of sodium paratungstate in determining, 170
- Nitration of ortho-, meta-, and paranitrobenzoylparaanisidines, 185
- products of dimethylparatoluidine, absorption spectra, 250
- Nitrides, preparation by reduction of alkaline cyanides, 119
- Nitrite and nitrate assimilation, 47
- Nitrites, action of hydrazine sulphate on, and determining nitrogen in, 210
- of alkylammonium series, 279, 304
- of bases of pyridine and quinoline series, 228
- of primary, secondary, and tertiary ammonium bases, 253
- Nitro-derivatives obtained by action of nitric acids on alcohols, constitution, 173
- of alcohols, constitution, 258
- Nitroamines, transformation and relation to substitution in benzene derivatives, 144
- Nitrogen, active modification, 276
- and carbon in organic compounds, determining, 223, 316
- chemical modification produced by electric discharge, 249
- compounds, 236, 243, 265
- derivatives of phthalic acid, 318
- economy of, and production of ammonia by peat, 11
- in nitrites, determining, 210
- industrial manufacture of pure, 282
- spectra of elements and compounds excited by, 276
- pentoxide in nitrates, use of sodium paratungstate in determination, 170
- Nitrohydroazo-compounds, alkaline condensations of, 250
- 3-Nitroorthoxylene, 315
- Nitrotyrrol, 11
- Nitroso-compounds, metallic, 96
- Nitrosoazides of dipentene, *d*-limonene, and *l*-limonene, 22
- Nivière, J., action of isobutylamine and diisobutylamine on α -bromobutyric acid, 84
- North, H. B., action of sulphuryl chloride on metals, 174
- Northampton Polytechnic Institute, 135
- Northern lights, 12
- Nottingham, University College, 129
- Noyes, W. A., "Organic Chemistry for the Laboratory" (review), 24
- Numbers, theory of partitions of, 16
- OBERMAIER, C. J., and A. Gutbier. (See Gutbier, A.)
- Obituary, Albert Cooper, 103
- Albert Ladenburg, 117
- Oddo, B., determination of active hydrogen in organic molecules, 186
- Odling, Prof., presentation of Faraday Medal to Pro Rikarda, 8

- Ohl, A., and G. Jantsch. (See Jantsch, G.)
- Oil, coccoanut, Shrewsbury and Knapp's process for estimating, 243
- emulsions, properties of, 17
- in spices, &c., estimation of small quantities of essential, 304
- of Dalmatian white thyme, essential, 302
- of Myrica Gale, L., composition of essential, 241
- of Origanum hirtum, Link, essential, 302
- of Pinus longifolia, constituents, 266
- seeds from French West Africa, composition, 174
- Oils, essential, quantitative determination of ketones in, 169
- Oliveri, F., equilibrium of solutions of iodine in organic substance, 12
- Optical dispersion, 2.9
- glasses, making, 255
- Optically active substances which contain no asymmetric atom in the molecule, 153
- Organic compounds at boiling-point, influence of constitution on molecular volumes of, 151, 166, 187, 199
- determining carbon and nitrogen in, 225, 316
- matter, complete destruction, 138
- Organo-magnesium compounds, action on methylacetylpyrrolate, 193
- Orienting influence of antimonious substituents in benzene nucleus, 285
- Origanum hirtum, Link, essential oil of, 302
- Ortho-nitrobenzylparaausidine, nitration, 185
- Orthoxylene derivatives, 315
- Orton, K. J. P., and H. King, chlorination of aylanilides, 22
- relation of velocity of chlorination of aromatic compounds to constitution, 22
- Osazones, preparation and phototropism, 120
- Ostrowskij, I., and T. Zerewitinoff. (See Zerewitinoff, T.)
- Ostwald Wilhelm, "Introduction to Chemistry" (review), 35
- "Über Katalyse" (review), 118
- Wolff, and K. Schorr. (See Schorr, K.)
- Oxford University, 121
- Oxide, cuprous, solubility in aqueous ammonia solutions, 230
- ferroalleric, 96
- ferrous, titration in silicates by Pebal-Dölter's method, 47
- Oxides, metallic, action of thionyl chloride on, 185
- Oxidising agents, action on iso pyromucic acid, 174
- formation in atmospheric air by ultra-violet rays, 162
- Oxime of cyclohexanone-4-carboxylic acid, molecular configuration, 302
- Oximes, cyclic, catalytic reduction, 59
- obtained with ethyl, methyl, and dimethylbenzoylactic ethers, 50
- N-phenyl ethers of, researches on, 45
- Oxygen compounds of iodine, action of hydrogen peroxide on, 318
- determination, 185
- of ethers, basic properties, 119
- Oxyhydroquinone derivatives, 193, 234
- Oxyindoxyl, constitution, 209
- preparation from unsubstituted azoic or hydr. azoic acids, 193
- researches on, 11, 137
- Oxy- β -methylthiophenes, 293
- Oxythiophenes, 162
- Ozonair, Ltd., announcement, 196
- Ozone, decomposition of dry, 242
- physiological influence, 301
- PAAL, C., influence of foreign substances on activity of catalysers, 47
- Padoa, M., decacyclene and its action on graphite, 12
- and L. Santil, influence of auxochromes on phototropism, 234
- preparation and phototropism of some osazones, 120
- Paine, H. H., rate of coagulation of colloidal copper, 139
- S. G., and A. Hardeo. (See Harden, A.)
- Palazzo, F. C., and R. Liverani, synthesis of pyrazolones of a compound of γ -pyrone, 210
- Palladium and sodium hypophosphite, hydrogenation by precipitated, 119
- hydrogenation in presence of divided, 193, 209
- Paniker, R., and E. Stiasny, acid character of gallotannic acid, 230
- Paraffin hydrocarbons, lower limit of inflammation of mixtures with air, 279
- Paramethoxylaldehyde and its occurrence in root of chlorocodon, 251
- Parametric integrals, class of, and application in Fourier series, 13
- Paranitrobenzylparaausidine, nitration, 185
- Paraoxybenzylamine, 245
- Parapara-diethylmethane, action of methylene chloride on, 47
- Paraphenylenediamine reaction and peroxyl diastase of cow's milk, 36
- Parker, J. G., and J. R. Blockley, value of non-tannins in formation of leather, 291
- Parravano, N., and P. de Cesaris, arsenides of tin, 43
- Parry, E. J., note on malefern, 305
- Partington, J. R., "Higher Mathematics for Chemical Students" (review), 95
- temperature-coefficient of electrical conductivity of hydrogen chloride in alcoholic solution, 266
- ane R. T. Hardman. (See Hardman, R. T.)
- and A. Lapworth. (See Lapworth, A.)
- Pascal, P., utilisation of magnetic field for determining constitution, 245
- to determine composition, 257
- Paschke, F., and E. Wedekind. (See Wedekind, E.)
- Patterson, T. S., and H. H. Montgomerie, influence of neutral solvents on velocity of reaction, 286
- Pawlewski, B., colour and constitution, 43
- Pear trees, glucoside in leaves of, 197
- Peat, production of ammonia and economy of nitrogen by, 11
- Pebal-Dölter's method for titration of ferrous oxide in silicates, 47
- Pélabon, H., metallography of the system selenium-antimony, 186
- Pelly, R. G., and E. Goulding. (See Goulding, E.)
- Perbromides and periodides of metals of alkaline earths, 210
- Perkin, A. C., myricetin, 242
- oxidation products of hydroxybenzoic acids, 22
- W. H., and F. S. Kipping. (See Kipping, F. S.)
- and W. J. Pope, optically active substances which contain no asymmetric atom in the molecule, 153
- Perkin, W. H., jun., and W. J. Pope, optically active derivatives of 1-methylcyclohexylidene-4-acetic acid, 230
- Pernitrosocamphor, constitution, 278
- Peroxydiastase of cow's milk and paraphenylenediamine reaction, 36
- Pertz, Miss D. F. M., and F. Darwin. (See Darwin, F.)
- Petrenko, G. J., and A. S. Fedorow, compounds of silver with cadmium, 209
- Petroleum mixtures, examination, 305
- Petroleums, determining density of heavy, 267
- Pfeiffer, P., alkyl compounds of stannous series, 60
- pyridine compounds of tin haloids, 161
- Pharmaceutical Society, School of Pharmacy of, 124
- Phenol derivatives containing a mobile nitro-group, synthesis with, 279
- synthesis of diethylcyclohexadiene from, 286
- Phenols, catalytic oxidation by leric salts, action of acids on, 15
- Phenoxthine, 119
- Phenylalkylisoxazolones obtained with ethyl, methyl, and dimethylbenzoylactic ethers, 59
- 2-Phenyl 1:3-benzoxazine-4-one, action of ammonia and amines on, 20
- β -Phenylethyl isocyanate, 228
- Phenylisopropyl ketone reactions, 252
- Phenylisoxazolone, azomethines derived from, 84
- Phenyl paramethoxystyryl ketone dibromide, elimination of bromine from, 23
- Philippe, L. H., α -glucodecose and glucodecitol, 113
- Phosphate, soil, effect of ignition, on, 191
- Phosphorus and manganese, ferromagnetic compounds, 270
- in milk, gravimetric estimation, 244
- luminescence of, 12
- syntheses with yellow, 161
- pentachloride, action on optically active hydroxy-acids and esters, 250
- sulphur compounds, 60
- Photolysis of alcohols, acid anhydrides, ether oxides, and ether salts by ultra-violet rays, 197
- Phototropism, influence of auxochromes on, 234
- of hydrazones of turfurol, 258
- Photography, studies in, 2.8
- Phthalylhydrazides, polymorphic, 21
- Physical properties of substances, general relation between, 293
- Society, 231, 254, 285
- Society's Annual Exhibition, 227, 281
- Pickering, S. U., copper salts and their behaviour with alkalis, 256
- cuprylgallates, 21
- Pickles, S. S., composition of essential oil of Myrica gale, L., 241
- essential oil of Dalmatian white thyme, 302
- of Origanum hirtum, Link, 302
- Pictet, A., and A. Gams, synthesis of berberin, 197
- and L. Ramseier, constituent of coal, 233
- Pigonewsky, G., and L. Tchougaeff. (See Tchougaeff, L.)
- Pinacone, acetylenic, catalytic isomerisation, 59
- products of hydrolysis of raw and pure, 258
- quantitative dehydration of pure, 36
- Pinus longifolia, constituents of oil of, 266
- Pipes, copper water, 96
- Pisovachi, E., negative case of indigoid condensation, 119
- Piutti, A., "Ricerche Sull' Elido" (review), 209
- Plancher, G., and U. Golacicchi, new oxidation of α -methyl indol, 13
- Plant chemistry, 109
- Plants, Indian solanaceous, active constituents, 266
- Platinum group, discovery of new element, probably of, 283
- Pleuroutus cretaceus, 145
- Poizar, L., and A. Seyewetz. (See Seyewetz, A.)
- Polariscopes, reflecting, 254
- Polypeptides of α -amino- α -nonoic acid, synthesis with glycine, alanine, leucine, asparagine, and aspartic acid, 230
- Poma, G., and G. Gabbi, binary systems of chlorides of monovalent metals, 12
- Pope, F. G., and H. Howard, indicators of methyl-red type, 228
- W. J., and W. H. Perkin. (See Perkin, W. H.)
- and W. H. Perkin, jun. (See Perkin, W. H., jun.)
- and J. Reed, dihydroxydihydrindamine and its resolution into optically active components, 278
- Porcelain tubes, gases evolved by walls of, 59
- Porlezza, C., and L. Marino. (See Marino, L.)
- Porometer, 16
- Porritt, A., and W. O. R. Holton. (See Holton, W. O. R.)
- Porter, R. P., "The Ten Republics" (review), 244
- Pöschel, D. V., "Einführung in die Kolloidchemie" (review), 317
- Poetma, S., and A. Smits. (See Smits, A.)
- Potassium barium orthosulphate, 244
- orthosulphate, 209
- cyanide, titration in presence of potassium ferrocyanide, 209
- ferrocyanide, preparation of pure, 221
- permanganate, estimation of small amounts of calcium by means of, 171
- Pouget, I., and D. Chouchak, colorimetric determination of phosphoric acid, 174
- Power, F. B., and T. Callan, constituents of seeds of Casimiroa edulis, 277
- and H. Rogerson, chemical examination of root of Ipomoea orizabensis, 314
- Pozzi-Escott, E., rapid detection of elements the sulphides of which are precipitated by H_2S in acid solution, 245
- Prandl, W., and H. Manz, action of calcium fluoride on vanadium pentoxide, 233
- Pratt, D. S., E. M. Chamor, and H. W. Redfield. (See Chamor, E. M.)
- L. A., and C. James. (See James, C.)
- Precipitates, lead carbonate, equilibria with, 222
- Pribram, R., and A. Franke, condensations by ultra-violet light, 47
- Priestley, Joseph, memorial to, 269
- Pring, J. N., and J. R. Curzon, influence of physical condition of metals on cathodic overvoltage, 316
- and D. M. Fairlie, methane equilibrium, 315
- synthesis of hydrocarbons at high temperatures, 239
- Pritham, H. C., fusions, 190

- Probeck, E., report on method of determination of glycerol, 46
 Propylammonium nitrite and decomposition by heat, 304
 Propylene diammonium, halogen aurates of, 48
 Pseudomorphine, preparation by mineral catalysis, 36
 Purvis, J. E., absorption spectra of triketohydrindene hydrate and derivatives, 254
 of various chlorine and bromine derivatives of benzene and of toluene, 240
 of various iodine derivatives of benzene and toluene, 287
 ultra-violet absorption spectra of vapours of various organic substances, 115
 Pyman, F. L., aminoalkylglyoxalines, 285
 isoquinoline derivatives, 239
 synthesis of histidine, 228
 Pyrazones of a compound of γ -pyrone, synthesis, 210
 Pyridine and ammonia, separation and determination, 193
 chlorine derivatives, 241
 compounds of tin halide, 161
 series, nitrates of bases of, 228
 pentachlororides, 47, 72
 Pyridio-pentachlororides, 209
 pentachlororides, 198
 Pyrometry, stellar, 10
 γ -Pyrone, synthesis of pyrazolones of a compound of 210
 Pyrrol derivatives, action of aldehydes on, 282
- QUARTZ** mercury lamps, ultra-violet radiations, 185, 197
 Quercite, polyphosphoric ethers of, 204
 Quinoline series, nitrates of bases of, 228
 Quinonemides, 279
- RABAUT, C.**, and J. Aloy. (See Aloy, J.)
 Rabbits, cholesterol content of liver of, under various diets and during inactivation, 301
 Radiations, ultra-violet, of quartz mercury lamp, 185, 197
 which decompose water, 59
 Radio-activity as a kinetic theory of a fourth state of matter, 110
 Radium emanation, action on thorium salts, 163, 175
 in gases from springs at Colombières-sur-Orb, 293
 C., ionising radiations emitted by, 84
 Rakshit, J. N., and P. C. Ray (See Ray, P. C.)
 Ramsay, Sir W., action of niton (radium emanation) on the salts of thorium, 175
 Presidential Address to British Association, 97
 Ramseyer, L., and A. Piclet. (See Piclet, A.)
 Rankin, G. A., and E. S. Shepherd. (See Shepherd, E. S.)
 Raoult, F., and M. Hanriot. (See Hanriot, M.)
 Ray, P. C., and J. N. Rakshit, nitrates of alkylammonium series, 279, 304
 trimercuridiethylammonium nitrite, 241
 Rays, ultra-violet, action on lactic acid, 24
 Raynaud, M., and O. de Coninck. (See de Coninck, O.)
 Reaction, influence of neutral solvents on velocity of, 286
 Reactions, use of liquid ammonia in chemical, 293
 Read, A. A., and J. O. Arnold. (See Arnold, J. O.)
 J., and W. J. Pope. (See Pope, W. J.)
 Reckleben, H., and J. Scheiber. (See Scheiber, J.)
 Redfield, H. W., E. M. Chamot, and D. S. Pratt. (See Chamot, E. M.)
 Reduth School of Mines, 136
 Reed, L., approximate estimation of starch by iodine, 244, 271
 Refractometer, Féry, 70
 Reichenheim, O., "Über die Spektren der Anodenstrahlen" (review), 71
 and E. Gehrcke. (See Gehrcke, E.)
 Reissert, A., and H. Holle, sulphur and nitrogen derivatives of phthalic acid, 318
 Residual affinity and chemical composition, relation between, 265
 Resin, Dammar, properties of different varieties, 119
 Reverdin, F., nitration of *o*-, *m*-, and *p*-nitrobenzyl-*p*-anisidines, 195
 and A. de Luc, constitution of monomethyl ether of Weselsky and Benedikt's dinitrohydroquinone, 294
 Reynolds, W. C., and W. H. Taylor, decomposition of nitric acid by light, 315
 Rhodium, electrical properties, 293
 Richard, A. H., dimethylpentene produced by combustion of dimethylacetic acid, 174
 Richards, Prof., fundamental properties of the elements, 7
 T. W., and O. Högnschmid, revision of atomic weight of calcium, 182, 199
 Riedel, W., and C. Tubandt. (See Tubandt, C.)
 Rivett, A. C. D., determination of moisture in butter, 261
 Roberts, E., "Famous Chemists" (review), 256
 E. J., separation of cerium by potassium permanganate, 210
 Robinson, C. S., and H. O. Jones, complex thio-oxalates, 287
 H. H., constituents of oil of Pinus longifolia, 266
 J. E., and C. James. (See James, C.)
 R., and E. Hope. (See Hope, E.)
 Rogerson, H., and F. B. Power. (See Power, F. B.)
 Röntgen Society, 255, 291
 Rosanoff, M. A., L. Gulick, and H. K. Larkin, preparation of acetamide, 1
 Roscoe, Sir H. E., and C. Schorlemmer, "Treatise on Chemistry" (review), 231
 Rosenhain, W., making optical glasses, 255
 Rosenheim, A., constitution of metatungstates and tungstic acid borates, 43
 Rosenstahl, A., role of affinity in dyeing, 36
 Roshdestwasky, A., and W. C. M. Lewis, electro-chemistry of solutions in acetone, 280
 Rost, H., and G. Darzens. (See Darzens, G.)
 Royal Institute of Public Health, Berlin Congress, 222
 Institution, 6, 234, 282, 306
 Photographic Society, 255
 Society, 16, 238, 248, 264, 274, 301
 of Arts, 12, 234
 medals, 12
 mine rescue apparatus, 6
 Rubber, determining amount of soluble part clea in raw, 305
 Rubidium, radiation of, 47
 Rubidium, hydrates of, 17
 Ruff, O., and A. Heinzelmann, uranium hexafluoride, 221
 and H. Lickert, vanadium bromides, 233
 Ruhemann, S., triketohydrindene hydrate, 229
 Russell, A., maximum value of electric stress between two unequal spherical electrodes, 288
 Rusting of metals, 241
- SABATIER, P.**, and A. Mailhe, catalytic decomposition of formic acid, 11
 new methods of preparing benzylamines and hexahydrobenzylamine, 174
 Saha, H., and K. N. Choudhuri, action of ammonia on mercurous nitrate, 210
 St. Andrews University, 131, 133
 address of Chemical Society to 18
 Salts, influence of dissolved on partition of a substance between two solvents, 174
 inorganic, new, 23
 of dithiocarbonalkylamine acids, 306
 Saltpetre, formation of conversion, from point of view of phase law, 119
 Salway, A. H., chemical examination of Calabar beans, 285
 synthesis of 4:6-dimethoxy-2- β -methylaminoethylbenzaldehyde, 21
 Sanchez, J. A., quantitative separation of iron and manganese, 257
 Sander, monazite, analysis, 197
 Sanders, J. M., convenient method for determining density of heavy petroleum, 267
 Sandonini, C., thermic analysis of binary mixtures of chlorides of monovalent metals, 120
 of mixtures of copper chloride with chlorides of monovalent elements, 12
 and G. Scarpa, thermic analysis of binary mixtures of chlorides of divalent metals, 210
 Santi, L., phototropism of hydrazone of furfural, 258
 and M. Padoa. (See Padoa, M.)
 Santolin estimation, 257
 Sazanoff, P., and V. Kohlschütter. (See Kohlschütter, V.)
 Scagliarini, G., and R. Ciusa. (See Ciusa, R.)
 Scarpa, G., and C. Sandonini. (See Sandonini, C.)
 Schaeffer, J. A., and J. H. James. (See James, J. H.)
 Scheffera, G., "Lehrbuch der Mathematik" (review), 35
 Scheiber, J., and H. Reckleben, determination of solid antimony hydride, 36
 of solid hydrogen arsenide, 36
 Schoeller, W., W. Schrauth, and R. Struensee. (See Schrauth, W.)
 Schorlemmer, C., and Sir H. E. Roscoe. (See Roscoe, Sir H. E.)
 Schorr, K., and W. Ostwald, "Das Edelem" (review), 149
 Schrauth, W., W. Schöeller, and R. Struensee, complex mercury compounds of cinnamic acid ester and cinnamic acid, 47
 Schreiber, H., and W. C. Taber, method for determination of tin in canned foods, 66
 Schröder, K., preparation of pure potassium ferrocyanide, 221
 Schwalbe, "Die Chemie der Cellulose" (review), 10
 Schwere, F., density of liquid sucrose and of its solutions in water, 228
 Segalier, D., relative activities of certain organic iodo-compounds, 288
 Selby, F. J., analysis of tidal records for Brisbane for 1908, 276
 Selenium-antimony, metallo-graphy of system, 185
 Sell, W. J., chlorine derivatives of pyridine, 241
 Semicarbazones and hydrazones of camphorquinone, absorption spectra of isomeric, 242
 Sen, H. K., and B. B. Dey. (See Dey, B. B.)
 Senderens, J. B., catalytic preparation of aromatic ketones, 294
 J. J. Aboulenc, catalytic etherification of aromatic acids, 137
 of dibasic acids, 233
 preparation of ether salts of acids of formic acid series, 84
 Sénéchal, A., and A. Colin. (See Colin, H.)
 Senier, A., and Rosalind Clarke, studies in phototropy and thermotropy, 278
 Seyewetz, A., and L. Poizat, direct preparation of compounds of sulphonic derivatives with mineral and organic bases, 62
 Shaw, H., and A. Fowler. (See Fowler, A.)
 Sheffield University, 130
 Shebourn, E. T., J. H. Coste, and E. R. Andrews. (See Coste, J. H.)
 Shen, B., and A. Findlay. (See Findlay, A.)
 Shepherd, E. S., and G. A. Rankin, ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, 103
 Shrewsbury, H. S., note on a counterfeit gold coin, 243
 and A. W. Knappe, notes on Shrewsbury and Knapp's process for estimating coconut oil, 243
 Sidgwick, N. V., and E. G. Laws. (See Laws, E. G.)
 Sievers, A., and B. Bergner, tantalum, tungsten, and hydrogen, 233
 Silbert, P., and G. Ciamician. (See Ciamician, G.)
 Silberrad, O., improved Soxhlet condenser, 54
 Silica, behaviour of fused, at high temperature, 77, 86
 cubical expansion of fused, 283
 standard of length, 17
 Silicates, detection, 295
 hydrothermal, 246
 titration of ferrous oxide by Pebal-Döbler's method, 47
 Silicon, amorphous, 12
 sulphides, 12
 Silver and cadmium compounds, 209
 and calcium, alloys, 53
 coin, composition of a false, 190
 determination by electrolytic separation from ammoniacal oxalate solution, 36
 estimation by electro-deposition from an ammoniacal solution of the oxalate, 193
 chloride, reduction, 173
 Simmonds, C., note on determination of small quantities of methyl alcohol, 305
 Simonsen, J. L., reactions of gum kino, 22
 Sinalhe iron of ancient origin, 275
 Sir John Cass Technical Institute, 136, 184, 281
 Slade, R. E., studies of ammonium solutions, 253
 Smedley, Ida, condensation of crotonaldehyde, 228
 Smiles, S., and H. Christopher. (See Christopher, H.)
 and H. T. Clarke. (See Clarke, H. T.)
 and Effie G. Marsden. (See Marsden, W. E. G.)
 Smirnow, W. J., and N. S. Kuroskow, definite compounds with varying composition of the solid phase, 221
 Smith, S. W. J., W. White, and S. G. Barker, magnetic transition temperature of cementite, 283
 Smits, A., and S. Postma, compounds of ammonia and water, 210
 Soap, estimation of water in, 247
 Society of Chemical Industry, 211, 243, 299

- Society of Public Analysts, 243, 304
- Sodium and nickel, and sodium and cobalt oxalates, stability of double, 278
- derivative of benzyl cyanide, action of anisic and piperonyl aldehydes on, 186
- ypophosphite and nickel, hydrogenation by means of, 119
- and palladium, hydrogenation by precipitated, 119
- hyposulphite cryoscopy in fused, 293
- ketones, syntheses of β -substituted diketones, ketonic ether salts, and enolic ethers by means of, 173
- palmitate, palmitic acid, 239
- paratungstate, use in determination of carbon dioxide in carbonates and nitrogen pentoxide in nitrates, 170
- peroxide, action on bismuth salts, 36
- Soil phosphates, effect of ignition on, 191
- Solanum dulcamara, fruit of, 2
- Solutions, application of Kirchhoff's equation to, 241
- influence of solvent on position of absorption bands in, 249
- metallic solid, formation by diffusion in solid state, 120
- theories of, 104
- theory and heats of, 293
- Solvents, ionisation of non-aqueous, 228
- Sornet, R., and M. D'elapine. (See D'elapine, M.)
- Sosman, R. B., and A. L. Day. (See Day, A. L.)
- Soukup, A., and J. Hanus. (See Hanus, J.)
- Soxhlet condenser, improved, 54
- Spartein, 59
- Spectra, absorption, of chlorine and bromine derivatives of benzene and of toluene, 240
- of iodine derivatives of benzene and toluene, 287
- of isomeric hydrazones and semicarbazones of camphorquinone, 242
- of nitration products of dimethylparatoluidine, 250
- of triketohydrindene hydrate and derivatives, 234
- studies of, 269
- of elements and compounds excited by nitrogen, 276
- ultra-violet absorption, of vapours of various organic substances, 115
- Spectrum, iron flame, and those of sun-spots and lower-type stars, 275
- of cyanogen, and its occurrence in carbon etc, 276
- Swan, conditions of, production, 293
- Spices, essential oil in, estimation of small quantities, 304
- Spring, L. V. W., method for nickel-zinc separation in German silver and other alloys, 58
- Squintani, V., and L. Marino. (See Marino, L.)
- Stähler, A., and F. Bachran, titanium, 252
- Stanley, F., "Lines in Arc Spectra of Elements" (review), 244
- Stansfield, E., forms of gas-pressure regulators, 3
- Stanton, T. E., mechanical viscosity of fluids, 17
- Starch, action of hydriodic acid on, 137
- approximate estimation by iodine, 244, 271
- Starck, G., new quantitative determination of fluorine, 35
- Starling, W. W., and G. Barger. (See Barger, G.)
- Stars, lower-type, and sun-spots, iron flame spectrum and those of, 275
- Staudinger, H., and H. W. Klever, preparation of isoprene from terpene hydrocarbons, 186
- Steel and iron metallurgy, progress in, 192
- sulphur in, volumetric estimation, 298
- vanadium in, colorimetric method for, 194, 202
- vanadium in, determination, 180
- corrosion, influence of carbon and other elements on, 142, 155
- gases contained in, 11
- nickel in, comparison of methods for determination, 168
- Steels, carbon in, employment of combustion under pressure to determine, 197
- Steele, V., action of hydrogen cyanide on carvone hydro-sulphide, 253
- and A. Lapworth. (See Lapworth, A.)
- Steenbock, H., improvement in Wiley method for determining melting-points of fat, 15
- Stellar pyrometry, 10
- Stereoisomerism, of cyanodihydrocarvone, 253
- Stereoisomerism, new variety, 242
- Stevens, H. P., and C. Beadle. (See Beadle, C.)
- Stewart, A. W., and R. Wright, studies of absorption spectra, 269
- Stiasny, E., and R. Paniker. (See Paniker, R.)
- Stock, A., and H. Blumenthal, tellurium carbide, 161
- Stollé, R., aldehyde hydrazine, 48
- Stomata, method of estimating the aperture of, 16
- Stötter, H., and M. O. Forster. (See Forster, M. O.)
- Stress, effects of holes and semi-circular notches, on distribution of, in tension members, 254
- Struensee, R. W. Schrauth, and W. Schoeller. (See Schrauth, W.)
- Strutt, R. J., chemically active modification of nitrogen produced by electric discharge, 249
- further observations on the afterglow of electric discharge and kindred phenomena, 231
- and A. Fowler. (See Fowler, A.)
- Strychnine and brucine, researches on, 234
- modification of Malaquin's reaction for characterisation of, 119
- Stubbs, C. M., influence of inactive electrolytes on optical activity of *l*-malic acid in aqueous solution, 242
- Sublimation in a vacuum, apparatus for, 251
- Substance containing C, H, N, O, S, Cl, Br, I, analysis, 245
- containing C, H, O, N, analysis, 245
- containing C, H, O, N, S, analysis, 245
- Substances, general relation between physical properties of, 293
- in solution, molecular state of, 306
- Succinic acids, ketoglutaric acids and acid-aldehydes of, 150
- Sucrose, density of liquid, and of its solutions in water, 228
- Sudborough, J. J., and E. R. Thomas, separation of mixtures of organic acids by partial esterification, 237
- Sugden, Ruth, precipitation of aluminium hydroxide in granular form, 35
- Selman, L., address to Sir John Cass Technical Institute, 281
- Sulphate, chromic, and ions, 257
- Sulphates, cerium earth double, decomposition with alkali sulphates by fusion with charcoal, 179
- qualitative detection of elements which form insoluble, 234
- Sulphides, action of carbon oxychloride on natural and artificial, 11
- of elements which are precipitated by H_2S in acid solution, 245
- Sulphocyanide, ferric, catalysing action, 72
- Sulpho-esters R. CS. OR', 185
- Sulphonic derivatives, preparation of compounds of, with mineral and organic bases, 62
- Sulphur and tellurium, metallographic and photochemical investigations of the system, 246
- apparent reversibility of vulcanisation of caoutchouc by, 245
- boiling point, constancy of, 274
- derivatives of phthalic acid, 318
- in iron and steel, volumetric estimation, 298
- volatility of compounds containing, 257
- phosphorus, compounds, 60
- Sulphuretted hydrogen apparatus, 189, 256
- Sulphuryl chloride, action on metals, 174
- on tellurium, 43
- Sun-spots and lower-type stars, iron flame spectrum and those of, 275
- Surface tension, experiments, 254
- Sutherland, Maggie M. J., and G. G. Henderson. (See Henderson, G. G.)
- Sutton, F., "Systematic Handbook of Volumetric Analysis" (review), 71
- Swan spectrum, conditions of production, 293
- Swinton, A. A. C., application of second law of thermodynamics to living organisms, 255
- Syntheses with yellow phosphorus, 161
- Synthesis with phenol derivatives containing a mobile nitro-group, 279
- TABER, W. C., and H. Schreiber. (See Schreiber, H.)
- Taboury, F., and F. Bodroux. (See Bodroux, F.)
- and M. Godchot. (See Godchot, M.)
- Tannin in wine, determination, 133
- Tantalum, tungsten, and hydrogen, 233
- Tassily, G., alcoholysis of Japan wax, 133
- Taylor, Clara M., and T. H. Easterfield. (See Easterfield, T. H.)
- R. L., action of chlorine on alkalis and of carbon dioxide on bleaching powder, 265
- W. H., and W. C. Reynolds. (See Reynolds, W. C.)
- Tchougaeff, L., and C. Pigoulewsky, dithiocamphocarboxylic acid, 197
- Tellurium, action of sulphuryl and thionyl chlorides on, 43
- alleged complexity of, 19, 260
- and sulphur, metallographic and photochemical investigations of the system, 246
- carbide, 161
- Tellurium compounds, preparation of pure aromatic, 233
- Temperature coefficient of diffusion, 289
- high, work, general discussion on, 9
- Temperatures, high, methods of maintaining constant, 9
- Tension, surface, 254
- Terebenthene essence, hydrogenation, 36
- Ternary system $CaO-Al_2O_3-SiO_2$, 103
- Terni, A., and R. Ciusa. (See Ciusa, R.)
- Terpene hydrocarbons, preparation of isoprene from, 186
- Terpenes, contributions to chemistry of, 229, 266, 286
- Tetra-alkyl silicanes, 233
- Tetrachlororidides, 47
- Thallium and calcium alloys, 53
- and manganese alloys, 53
- Thallous hydroxide, 123
- Thermal phenomena, curious, 96, 118, 173
- Thermo-dynamics, application of second law of to living organisms, 255
- Thermometry, gas, recent advances in high-temperature, 51, 62
- Thermostats, 295
- and devices used in connection therewith, 307
- Thermotropy, studies in, 278
- Thionyl chloride, action on ethers of acid alcohols in presence of a tertiary base, 108
- on metallic oxides, 185
- on optically active hydroxy-acids and esters, 250
- on tellurium, 48
- Thio-oxalates, complex, 287
- Thiophenates, action of bromonitrobenzenes on, 294
- Thioxanthone derivatives, synthesis, 229, 280
- from aromatic disulphides, 223
- Thole, F. B., note on preparation of labile benzaldehyde-phenylhydrazones, 287
- and A. E. Dunstan. (See Dunstan, A. E.)
- and J. F. Thorpe, chemistry of glutaric acids, 263
- formation and reactions of imino-compounds, 240
- probable cause of elimination of a carboethoxyl group as ethyl carbonate by action of sodium ethoxide, 263
- Thomas, E. R., and J. J. Sudborough. (See Sudborough, J. J.)
- H. L., use of acetylene in laboratories, 72
- J. S., and F. G. Donnan. (See Donnan, F. G.)
- Thomlinson, J. C., estimation of santonin, 257
- Thompson, S. P., experiments in acoustics, 255
- harmonograph, 255
- and E. G. Coker, reflecting polariscopes, 254
- Thorium, detection and determination with iodic acid, 120
- emanation, molecular weight, 186
- α -particles emitted by, 239
- salts, action of radium emanation on, 163, 175
- carbonates, 150
- Thorp, E. L., and S. R. Trotman. (See Trotman, S. R.)
- Thorpe, Sir E., "Essays in Historical Chemistry" (review), 148
- J. F., and G. L. Blanc. (See Blanc, G. L.)
- Thorpe, J. F., and F. B. Thole. (See Thole, F. B.)
- Thorvaldson, T., and G. P. Baxter. (See Baxter, G. P.)
- and V. Cobb. (See Baxter, G. P.)
- Thulium, 73
- Thymic, white, essential oil of Dalmatian, 302
- Thymol, synthesis of a menthadiene from, 286
- Tian, A., radiations which decompose water, 59

- Tidal records for Brisbane, 1908, analysis, 276
- Tiede, E., and F. Fischer, distillation of tin in vacuo, 161
- Tiffeneau, M., monomethyl and dimethyl-3,4-dioxybenzylamine, 294
- and dimethyl-*p*-oxybenzylamine, 246
- p*-oxybenzylamine, 245
- Tilden, Sir W. A., presentation of Faraday medal to Prof. Richards, 8
- Tin and arsenic compounds, 24
- distillation in vacuo, 161
- haloids, pyridine compounds of, 161
- in canned foods, determination, 66
- arsenides, 43
- Titanium, 282
- sensitiveness of colorimetric determinations of, 48
- Titherley, A. W., and E. C. Hughes, action of ammonia and amines on 2-phenyl-1:3-benzoxazine-4-one, 29
- Titration of potassium cyanide in presence of potassium ferrocyanide, 209
- Tizard, H. T., "Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics" (review), 196
- Toluene, absorption spectra of chlorine and bromine derivatives of, 240
- of iodine derivatives of, 287
- Toxins, neutralisation by means of antitoxins, 39
- Traill-Taylor, memorial lecture, 255
- Trapnagen, F. W., electrolytic determination of copper, 69
- Treadwell, W. D., titration of potassium cyanide in presence of potassium ferrocyanide, 209
- Trialkylammonium nitrites, 228
- Triazo-group, 22
- Triethylammonium nitrite and its decomposition and sublimation by heat, 279
- Triketohydrindene hydrate, 229
- and derivatives, absorption spectra, 254
- Trimercurdiethylnammonium nitrite, 241
- Trimethyl ether, gallic acid, and pyrogallocarboxylic acid, action of nitric acid on, 230
- Trotman, S. R., and E. L. Thorp, "Principles of Bleaching and Finishing of Cotton" (review), 184
- Trotter, J. R., M. O. Forster, and J. Weintraub. (See Forster, M. O.)
- Tryptophan, betaine of, preparation and identity with alkaloid hypaphorine, 277
- Tsakalotos, D. E., basic properties of the oxygen of ethers, 119
- Tubandt, C., and W. Riedel, nickel superoxide, 246
- Tungsten, ductile, 34
- tactalium and hydrogen, 233
- Turner, Emily G., and J. Kenner. (See Kenner, J.)
- Turpeatine, Finnish, examination, 243
- Tutton, A. E. H., "Crystals" (review), 10
- Tyler, D., latent heats of vaporisation of mixed liquids, 231
- UNIVERSITY Tutorial College, 136
- Uramil and purpuric acid, analogues of, 229
- Uranium carbide, formula of, 119
- hexafluoride, 221
- Uranyl phosphates and amines, 47
- Urea, determination, 318
- new derivative, 245
- Ureins of *p*-oxyphenylaminoacetic and *p*-methoxyphenylaminoacetic acids, 29
- VALEUR, A., and C. Moureu. (See Moureu, C.)
- Van der Waals, J. D., "Die Zustandsgleichung" (review), 135
- Van Gelderen, F. M., and M. O. Forster. (See Forster, M. O.)
- Van Kumburgh, F., and G. Barger, preparation of betaine of tryptophan and its identity with alkaloid hypaphorine, 277
- Van't Hoff's hypothesis and the dissolved molecule, 137
- Vanadium and iron present together, volumetric determination, 209
- in iron and steel, colorimetric method, 194, 202
- in steel and iron, determination, 180
- fluorides, 233
- pentoxide, action of calcium fluoride on, 233
- Vaporisation of mixed liquids, latent heats of, 231
- Vapour densities, determining Hofmann's method, 259
- Vapours, metallic, absorption and dispersion in, 116
- of various organic substances, ultra-violet absorption spectra of, 115
- Vavon, G., hydrogenation of carvone, 145
- of essence of terebenthene, 36
- of limonene, 84
- Veit, T., and E. Wedekind (See Wedekind, E.)
- Veley, V. H., solution volumes of nitric acid, 309
- use of indicators for determining affinity values, 115
- Vernon, F. T., simple sulphuretted hydrogen apparatus, 256
- Vidal, J., and C. Astré. (See Astré, C.)
- Vienna, Technical Museum, 84
- Vigouroux, E., and A. Bourbon, alloys of nickel and zinc, 257
- Viguier, P. L., attempts to prepare tetrolic aldehyde, 306
- tetrolic aldehyde, 59
- Vila, M., and E. Pourneau. (See Pourneau, E.)
- Vogt, J. H. L., labradorite-norite with porphyritic labradorite crystals, 161
- Volatility of compounds containing sulphur, 257
- Von Engelhardt, K., and H. Ley. (See Ley, H.)
- Von Horvath, B., action of sulphur and thionyl chlorides on tellurium, 45
- Von Weimarn, P. P., "Grundzüge der Dispersoidchemie" (review), 317
- Vournasos, A. C., preparation of nitrides by reduction of alkaline cyanides, 119
- Vulcanisation of caoutchouc by sulphur, 245
- WADMORE, J. M., "Elementary Chemical Theory" (review), 24
- Waidner, C. W., and G. K. Burgess, constancy of sulphur boiling-point, 274
- Walden inversion, experiments on, 250
- Wales, University of, 124
- Walker, J., theories of solutions, address to Chemical Section of British Association, 104
- S. F., "Cold Storage and Ventilation on Board Ship" (review), 161
- W. O. and J. A. McRae, determination of halogens in organic compounds, 70
- Waller, E., curious thermal phenomenon, 173
- Walling, W. A. B., notes on setting of cement, 54
- Water and ammonia compounds, 210
- decomposition by metals, 84
- nitrites and nitrites in, determining, 119
- in, determination, phenolsulphonic acid method, 146, 159, 167, 178, 235
- of crystallisation, effect of continued grinding on, 313
- pipes, copper, 96
- radiations which decompose, 59
- softening, 174
- supply, 205, 215
- Watson, W., sensibility of eye to variations of wave-length, 18
- Wave-length, sensibility of eye to variations of, 18
- Wedekind, E., action of hydrofluoric acid on zirconium oxide, 161
- and F. Paschke, influence of the medium and of light upon the decomposition of quaternary ammonium salts, 96
- and T. Veit, ferromagnetic compounds of manganese, 233
- Weintraub, E., properties and preparation of the element boron, 157
- Weintraube, J., M. O. Forster, and J. R. Trotter. (See Forster, M. O.)
- Weizmann, C., and A. Hopwood (See Hopwood, A.)
- Wells, R. C., sensitiveness of colorimetric determinations of titanium, 43
- Wertenstein, L., ionising radiations emitted by radium C, 84
- Weselsky and Benedikt's dinitro-dihydroquinone, constitution of monomethyl ether of, 294
- West, G. D., resistance to motion of a thread of mercury in a glass tube, 276
- Weston, F. E., "Mauvel Pratique d'Analyse Organique" (review), 71
- Weydert, L., and P. Bary. (See Bary, P.)
- Wheeler, R. V., and M. J. Burgess. (See Burgess, M. J.)
- White, A. S., and P. G. Donnan (See Donnan, F. G.)
- E. A., German university degrees, 159
- G. F., and E. C. Biagham. (See Biagham, E. C.)
- W. S. W. J. Smith, and S. G. Barker. (See Smith, S. W. J.)
- Wiesbaden, Chemical Laboratory Fresenius, 133
- Wiley method for determining melting-points of fat, 15
- Wilks, W. A. R., absorption of halogens by dry slaked lime, 316
- Williams, Katharine I., cooking and chemical composition of English fish, 271
- R. S., and W. T. Hall. (See Hall, W. T.)
- Wiladon, B. H., F. D. Chattaway, and C. L. Cumming. (See Chattaway, F. D.)
- Wilson, F. J., and A. A. Boon. (See Boon, A. A.)
- Wine, tannin in, determination, 138
- Woltereck, H., production of ammonia and economy of nitrogen by peat, 11
- Wolverhampton Municipal Science and Technical School, 136
- Worden, E. C., "Nitrocellulose Industry" (review), 148
- Wren, Gertrude H., and A. W. Crossley. (See Crossley, A. W.)
- Wright, E., simplified combustion calorimeter, 231
- R., and A. W. Stewart. (See Stewart, A. W.)
- Wunder, M., and B. Jeanneret, action of syrupy phosphoric acid on alloys obtained in an electric furnace, 118
- Wünsch, D. F., and F. D. Chattaway. (See Chattaway, F. D.)
- X-RADIATION, homogeneous fluorescent, of second series, 231
- X-ray, energy of, 291
- Xanthates, metallic, decomposition by heat, 119
- YEAST, autofermentation, action of dissolved substances on, 301
- Young, W. H., class of parametric integrals and application in theory of Fourier series, 18
- Yttrium earths, fractionation by means of succinates, 203
- ZACHARIAS, J., "Elektrochemische Umformer—Galvanische Elemente" (review), 185
- Zelinsky, N., dehydrogenation by catalysis, 318
- Zerewitinoff, T., and I. Ostromisslensky, bismuth oxide as a reducing agent, 233
- Zerner, E., ethyl derivatives of acetone, 72
- Zinc and magnesium compound, isolation, 276
- and nickel alloys, 257
- nickel, separation in German silver and other alloys, 58
- nitrate in zinc powder and in commercial zinc, 24
- peroxyde, zinc monoxide, zinc peroxyde, 162
- Zirconium oxide, action of hydrofluoric acid on, 161
- Zymase, character of, 177

122627

Author Chemical News

P
Chem & Phys

Title

DATE

Vol. 104 1911

University of Toronto
Library

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

STORAGE

Acme Library Card Pocket
Under Pat. "Ref. Index File"
Made by LIBRARY BUREAU

